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MANUAL OF METALLURGY.

A MANUAL

OF

METALLURGY.

ILLUSTRATED BY 100 ENGRAVINGS.

BY

GEORGE HOGARTH MAKINS, M.R.C.S. F.C.S.

LATE ONE OF THE ASSAYERS AND REFEREE TO THE BANK OF ENGLAND;
AND ASSAYER TO THE ANGLO-MEXICAN MINTS;
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SECOND EDITION,
REWRITTEN AND MUCH ENLARGED.

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PREFACE.

A NEW edition of this Manual having been for some time called for, the Author has thoroughly revised it, and re-written much which in the progress and improvements effected in metallurgic operations, had become obsolete or superseded. In doing this, he has added to its size, and introduced a large number of extra and useful illustrations; and he has, moreover, adopted in the chemical portions the nomenclature, atomic weights, &c. in accordance with present views, and now so universally employed.

The first edition was the substance of a short course of lectures delivered with regard to special requirements, but from other channels in which the book has circulated, the Author has in the present edition very much extended it, aiming at making it as useful as possible as a short comprehensive manual for the general student; and although by this he has put aside any special object, he believes he has not thus detracted from its usefulness to any, but, on the contrary, enhanced it; and again he has not thought it needful to alter the arrangement of the first edition, or materially the order in which the metals were therein considered.

Every one engaged in metallurgic pursuits must feel how much the science and practice of the various branches of these are indebted to such an author as Dr. Percy, the candour and impartiality of whose writings (the fruits of long experience) are only excelled by the exhaustive way in which each subject is treated by him, the latter fact, of necessity, rendering his works voluminous.

The Author of the present volume hopes that a moderately condensed one, in which the leading points connected with the principal metals are set forth, may be found useful.

He has to acknowledge his obligations to the author already named, also to Bruno Kerl's 'Handbuch' in German, and again to Mr. Crookes' careful translation of the same; to Phillips's 'Mining and Metallurgy of Gold and Silver,' and several other such standard works.

He would here thank his former colleague, Mr. D. C. Griffith (one of the Assayers to the Bank of England), for his valuable information upon lead-refining, desilverizing, &c., in which operations that gentleman has now had very considerable experience; and also his former pupil, Mr. James Napier, jun., for details of the Mexican plan of amalgamation, operations in which he was personally engaged at Guanaxuato; and, lastly, to those other friends who have kindly afforded information on special points in the various departments in which they are occupied.

January, 1873.

CONTENTS.

CHAP. PAGE
I. GENERAL PROPERTIES OF THE METALS 1
II. COMBINATIONS OF METALS WITH THE NON-METALLIC ELEMENTS 34
III. METALLIC SALTS AND ALLOYS 53
IV. OF HEATING-APPARATUS, FURNACES, ETC. 68
V. OF THE FUELS APPLICABLE TO METALLURGIC OPERATIONS . 109

NOBLE METALS :

VI. MERCURY 128
VII. SILVER 150
VIII. GOLD 220
IX. PLATINUM 291
X. PALLADIUM 307

BASE METALS :

XI. LEAD 312
XII. BISMUTH 342
XIII. COPPER 351
XIV. ANTIMONY 384
XV. URANIUM, TITANIUM, AND CHROMIUM 393
XVI. ARSENIC 402

CHAP. PAGE

BASE METALS (*continued*):

XVII. IRON AND STEEL 410
XVIII. MANGANESE AND COBALT 476
XIX. NICKEL 484
XX. TIN 491
XXI. ZINC AND CADMIUM 510
XXII. ALUMINIUM 529

BASE METALS OF THE SECOND DIVISION :

XXIII. MAGNESIUM 537

BASE METALS OF THE FIRST DIVISION :

XXIV. POTASSIUM AND SODIUM 541

XXV. THE PRINCIPLES OF ELECTRO-METALLURGY . . . 548

APPENDIX 570
INDEX 579

LIST OF WOOD-ENGRAVINGS.

FIG. PAGE
1 Wire-drawing bench 11
2 Specific-gravity balance 19
3 Specific-gravity bottle 21
4 Gravimeter 22
5 Mine; shaft, adit level, cross cuts, &c. 27
6 Mine: galleries, winzes, &c. 29
7 Reduction of oxides by hydrogen 41
8 Cleavage of cube to octohedron 57
9 Bunsen burner 70
10 Gore's gas melting furnace 73
11 Griffin's gas melting furnace 74
12 Siemen's gas producer 77
13 Siemen's regenerative furnace 79
14 Alcohol blast lamp 82
15 Black's blowpipe 84
16 Diagram of flame . . . . ib.
17 Blowpipe oxidizing flame 85
18 Blowpipe reducing flame 86
19 Blowpipe table and bellows 89
20 Blowpipe, Herapath's 90
21 Griffin's gas blast furnace 92
22 Wind furnace 93
23 Reverberatory furnace 95
24 Sefstrom's furnace 98
25 Daniell's pyrometer 124
26 Idrian mercury furnaces 130

FIG. PAGE
27 Butyrone mercury furnaces 133
28 Aludels . . . . ib.
29 Lansberg mercury apparatus front 136
30 Lansberg mercury apparatus section 137
31 Estimation of mercury 148
32 Mexican arrastre 159
33 Amalgamating barrel 164
34 Amalgamating barrel machine 165
35 Furnaces for distillation of silver amalgam . . . 167
36 Cupelling furnace for silver leads 169
37 Cupelling furnace plan with cupel, &c. . . . ib.
38 Cupel ring and frame 171
39 Cupel, with breast and gate shown . . . . . ib.
40 Cupel, section of . . . . ib.
41 Scorifier 189
42 Cupel for assaying operations 191
43 Cupel mould . . . . ib.
44 Cupel furnace, section 192
45 Cupel furnace, front view 193
46 Cupel furnace, gas (Griffin's) 196
47 Section of Watson's gas muffle furnace, front . . . 198
48 Section of Watson's gas muffle furnace, side . . . ib.
49 Front view Watson's furnace . . . . . . ib.
50 Assay furnace tools 199
51 Assay balance 201
52 Assay balance, with rider apparatus, &c. . . . 203
53 Apparatus for wet silver assays 212
54 Pipette cock for wet silver assays 213
55 Cradle for gold-washing 231
56 Roller quartz-crushing machine 234
57 Stamp and mortar 235
58 Amalgamating machine 237
59 Gas-parting apparatus 281
60 Matthey's platinum parting apparatus 284
61 Matthey's platinum parting apparatus cup, actual size . ib.
62 Black's balance 288
63 Deville's platinum refining furnace 299
64 Deville's platinum melting furnace 301
65 Lead reverberatory, section 319
66 Lead reverberatory, plan . . . . . . ib.

FIG.		PAGE
67	Blast furnace for lead	322
68	Blast furnace for lead, plan of base	ib.
69	Castilian or cupola furnace	324
70	Lead improving furnace, section	326
71	Lead improving furnace, plan	ib.
72	Pattinson's operation diagram	328
73	Pattinson's pots and furnaces	329
74	Pattinson's tools for operation	ib.
75	Bismuth liquation furnace	343
76	Copper calcining furnace	358
77	Copper ore furnace	359
78	Copper ore furnace, outline elevation	360
79	Mansfeld blast furnace for copper	370
80	Mansfeld blast-furnace receiving basins	371
81	Mansfeld reverberatory bed	372
82	Mansfeld refinery	373
83	Antimony liquation furnace	385
84	Marsh's arsenic detection apparatus	407
85	Iron blast-furnace	423
86	Iron blast-furnace in work	424
87	Iron blowing cylinder	426
88	Iron refinery, section	436
89	Iron refinery, plan of tuyeres, &c.	ib.
90	Puddling furnace, elevation	438
91	Puddling furnace, section	439
92	Steel cementing furnace	446
93	Bessemer Converter, back view, half in section	456
94	Bessemer Converter, side view	ib.
95	Tin reverberatory	495
96	Tin blast-furnace	496
97	Zinc furnace, English	511
98	Zinc furnace, Belgian, side view	513
99	Zinc furnace, Belgian, front view	ib.
100	Silesian zinc muffle	514

The reader is requested to correct the following Errata occurring in the text:—

Page	4	*for*	Cb	*read*	Cs, line 22
„	10	„	tenacity	„	tenuity, line 7 from bottom.
„	15	„	2 (in tenacity column)	„	?, line 13.
„	37	„	same	„	sum, line 5.
„	43	„	salt of copper	„	a salt of copper, line 10.
„	55	„	proportion	„	proportional, line 11 from bottom.
„	58	„	equivalents	„	atoms, in two last lines.
„	66	„	it as	„	that, line 12 from bottom.
„	67	„	Bollers	„	Bolley, in foot-note.
„	129	„	cupellous	„	cupreous, line 17.
„	136	„	Points	„	Ponts, line 14.
„	232	„	land	„	hand, line 17.
„	259	„	transmuted	„	transmitted, line 1.
„	263	„	Au 20	„	$Au_2 O$, line 2 from bottom.
„	312	„	silver ton	„	silver per ton, line 4 from bottom.
„	345	„	$B'''i$	„	Bi''', line 6 from bottom.
„	353	„	$2 Cu O_3$	„	$2 Cu CO_3$, line 9.
„	381	„	metal	„	nickel, line 21.
„	387	*dele*	soda		line 10.
„	468	*for*	Fe'''	„	Fe'', line 8 from bottom.
„	479	„	$M_2 On_3$	„	$Mn_2 O_3$, line 6 from bottom.
„	483	„	Fresny	„	Fremy, line 4 from bottom.
„	484	„	Magnesia	„	Manganese, line 9 from bottom.

METALLURGY.

CHAPTER I.

GENERAL PROPERTIES OF THE METALS.

The operations of the chemist have for their object either, on the one hand, the combination of diverse forms of matter, whereby new compound bodies are produced, or else, on the other, the separation of compounds already existing, so as to reduce them to simpler states; thus, by the latter method of proceeding, he will arrive at points where the process of separation is no longer practicable, although possibly this stop is put to the decomposing process by our want of means to carry it on in our present state of knowledge. The ultimate forms into which all compound bodies are resolvable are called 'elements.'

The elements at present known are about sixty-three in number, while of these no less than fifty are called 'metals.' Their study constitutes the science of Metallurgy, which, although by strict definition means the production of metals, will, throughout the following pages, be extended to as much of their chemistry also as relates to their less complex compounds. Indeed the rapid progress made in Metallurgy, both in the improvement of its older operations as well as in the devising and carrying out of new ones, is mainly due to chemistry.

As chemical changes, or reactions, as they are termed, are frequently somewhat complex, it is found convenient to be able to express the names of elements in short, and thus, by means of abbreviations, to construct formulæ of such changes, whereby the whole of any operation may at once be brought under the eye. These abbreviations, called symbols, are commonly made by employing the first letter of the Latin name of the element, or, where such initial letter is common to more than one element, then using the two first letters for the less important one.

Again, as each element is supposed to have a definite atomic weight, as it is expressed, or, in other words, a proportion as compared with the rest, in which it will enter into combination to form a compound body, such quantity has, until very recently, been called its 'equivalent'—a term expressing the fact that a certain weight of one body is just equivalent to, and will replace, a certain equally fixed weight of another in forming new combinations, the combining equivalent of the gas hydrogen forming the unit of the system of numbers. But as chemists have of late applied the terms 'equivalent' and 'equivalency' in a different sense, in accordance with recent chemical discovery, it is found better to designate such quantities as atomic weights, or combining proportionals.

But very little more than a century back the old writers on the metals stated their total number as six only, adding some four or five (of which zinc was one) which they termed semi-metals. In 1751, however, Cronstedt discovered nickel, and up to the end of that century Klaproth and others added a few more to the list; but during the present century, commencing with Davy's isolation of the metals of the alkalies and alkaline earths in 1808, discoveries have rapidly progressed; so that what were chemical rarities, as aluminium and magnesium for instance, are now in daily manufacture on the large scale. And again, during the last ten years or so, no less than four more new and well-defined metals have been brought to light by means of spectrum analysis.

The progress of chemical knowledge has led to more complete examination of these subjects. Thus, in the case of magnesium, which Davy failed to isolate, a later chemist, Bussy, succeeded in; and Sonstadt has of late rendered its production an ordinary operation. Similarly the red body, which even so accurate an experimenter as Wollaston stated to be pure titanium, has been shown by Wohler and Deville to be but a compound of that metal, they having, moreover, produced the steel grey metal itself. And, lastly, the researches of Crookes upon thallium, of Roscoe on vanadium, and the work of the late Dr. Matthiesen on metals and alloys generally, show fully the bearing and influence which refined chemical and physical knowledge exerts upon the operations of the metallurgist.

Of the known metals not more than about fourteen are employed in true metallic condition. In this list we may place—

Iron,
Copper,
Lead,
Zinc,
Tin,
Antimony,
Nickel,
Aluminium,
Magnesium,
Bismuth,
Gold,
Silver,
Mercury,
Platinum.

Then about twelve are extensively used in their compounds, and some of these for alloying purposes. These are—

Potassium,
Sodium,
Calcium,
Barium,
Lithium,
Manganese,
Arsenic,
Chromium,
Cobalt,
Cadmium,
Titanium,
Uranium.

While the twenty-four remaining are more or less rare.

The metallic elements may be first divided into two classes, noble and base: the noble metals being those whose compounds with oxygen are decomposable by heat alone; the base, those which retain oxygen at high temperatures.

There are several methods of classifying the metals, but perhaps the most useful and practical one is founded upon their analytical bearings; and upon this the following table is arranged, in which against each is placed its symbol and atomic weight, the names of those of less importance being printed in smaller type.

The base metals may be classed first, and in six divisions. The metals of the first division are characterised by very low specific gravity; they are very soft, and also fusible at low temperatures. They are so readily oxidised as to extract oxygen from water, with liberation of its hydrogen. Their oxides are soluble in water, and give it an alkaline reaction, as also are their phosphates and carbonates. Hence potassic carbonate will not precipitate solutions of other metals of this division (excepting lithium, and the precipitate produced in lithium will redissolve with slight heating or agitation). Neither hydrosulphuric acid (dihydric sulphide) nor sulphide of ammonium (ammonio-hydric sulphide) produce any precipitate.

This division contains five metals:—

	Symbol.	Atomic Weight.	
Potassium	K′	39·1	
Sodium	Na	23	
Lithium	L	7	
Rubidium	Rb	85·36	
Cœsium	C[illegible]	133	Cs.

In the second division some decompose water rapidly. Their oxides are more or less soluble in water, and render it alkaline; but the neutral carbonates and phosphates are insoluble: hence metals of this division are precipitated by potassic carbonate; they are not precipitated by hydrosulphuric acid (dihydric sulphide) nor by sulphide of ammonium (ammonio-hydric sulphide).

It contains four metals:—

Barium	Ba″	137
Strontium	Sr″	87·5
Calcium	Ca″	40
Magnesium	Mg″	24·3

In the third division those metals which have been isolated do not decompose water at ordinary temperatures without the addition of a weak acid or a slight rise of temperature. Their oxides and carbonates are insoluble in water, and hence potassic carbonate throws down a precipitate from their solutions. Sulphide of ammonium (ammonio-hydric sulphide) precipitates from them a hydrated oxide, and not a sulphide—in fact, acts just as pure ammonia would do. Hydrosulphuric acid (dihydric sulphide) gives no precipitate.

Thirteen metals come into this division, but ten of these are of small importance :—

Aluminium	Al'''	27·5
Chromium	Cr	52·5
Titanium	Ti	50

Glucinum or Beryllium	G''	9·5
Thornium	Th	238
Yttrium	Y	61·7
Zirconium	Zr	89·5
Erbium		112·6
Cerium	Ce	92
Lanthanum	La	96
Didimium	Di	94
Tantalum	Ta	182
Columbium or Niobium	Nb	94

In the fourth division, several of the chief decompose water at a red heat. Their acid solutions are not precipitated by hydrosulphuric acid (dihydric sulphide), but, if neutral, a partial precipitation will take place. Sulphide of ammonium (ammonio-hydric sulphide) completely precipitates alkaline or neutral solutions, and the division is distinguished from the third in this precipitate being a sulphide. It contains nine metals :—

Iron	Fe''	56
Nickel	Ni''	59
Cobalt	Co''	59
Manganese	Mn	55
Zinc	Zn''	65
Uranium	U	120

Vanadium	V	51·4
Thallium	Tl	204
Indium	In	75·6

Metals of the fifth division do not decompose water at any temperature. Hydrosulphuric acid (dihydric sulphide) precipitates them, whether acid, alkaline, or neutral; because the precipitated sulphides are insoluble in dilute acids or in alkaline sulphides. (In the latter, however, cupric sulphide is slightly soluble.) This precipitation by hydrosulphuric acid distinguishes this from the four preceding groups.

It contains four metals:—

Cadmium	Cd''	112
Lead	Pb''	207
Bismuth	Bi'''	210
Copper	Cu''	63·5

In the sixth division all the higher oxides of the metals have acid properties. Hydrosulphuric acid (dihydric sulphide) throws down their sulphides insoluble in acids, but soluble in alkaline sulphides, for they act as sulphur acids to the latter as bases. Hence they are soluble in sulphide of ammonium (ammonio-hydric sulphide), but may be reprecipitated by acids.

The metals are six in number:—

Tin	Sn^{iv}	118
Antimony	Sb'''	122
Arsenic	As'''	75
Molybdenum	Mo	96
Tungsten	W	184
Tellurium	Te	129

The second class of metals, termed noble, is distinguished more especially by their oxides being reduced by heat alone, and some, as oxide of gold for example, at a very low temperature. Their general chemical characters resemble those of the fifth and sixth divisions of the base metals; some have their sulphides soluble in sulphide of ammonium, and especially if it contains excess of sulphur; thus gold, platinum, and iridium, in this respect resemble division 6 of the base.

There are nine noble metals:—

Mercury	Hg	200
Silver	Ag′	108
Gold	Au	196·6
Platinum	Pt	197·1
Palladium	Pd″	106·5
Rhodium	Ro‴	104·3
Ruthenium	Ru	104·2
Osmium	Os	199
Iridium	Ir	197·1

The non-metallic elements may be divided according to their physical states in the following way:—

Gaseous Elements.	Symbol.	Atomic Weight.
1. Oxygen	O	16
2. Hydrogen	H	1
3. Nitrogen	N	14
4. Chlorine	Cl	35·5
5. Fluorine	F	19
Solids.		
1. Carbon	C	12
2. Boron	B	10·9
3. Silicon	Si	28
4. Sulphur	S	32
5. Selenium	Se	79·5
6. Phosphorus	P	31
7. Iodine	I	127
Liquid.		
1. Bromine	Br	80

A metal may be defined as a solid elementary body, which conducts heat and electricity through its substance perfectly, and has a peculiar condition of surface, whereby light is strongly reflected from it; and hence its surface is more or less lustrous. The latter character is generally so strongly marked that, in speaking in common language of any lustrous body, we say it has 'a metallic lustre.' It seems to be the result of perfect opacity, by which all rays are reflected from the surface; for, if we take finely divided gold or silver, we observe it to be a dull, sandy-looking body, yellow in the former, and grey in the latter case; but the least condensation of surface by rubbing with the smooth face of a hammer or a burnisher, will produce the necessary state of it for this reflexion of light.

The smoother the burnisher the better the surface. Thus the Birmingham button-makers generally use an agate burnisher as giving a smoother surface than a metal one. Electro deposits of gold or of silver when removed from the decomposing cell are perfectly dull and unmetallic in appearance, but a wire scratch brush brings up metallic lustre by laying the surface without penetrating into or removing metal.

The metals are nearly all perfectly opaque, even in thin leaves, although the small number possessing transparency may depend on our inability to bring such into a sufficiently attenuated state; for gold, which readily admits of this, is easily shown to transmit green light.

This may be very elegantly demonstrated by taking some twenty grains of fine gold, and fusing it in a convenient shallow vessel. This is to be removed from the furnace in a completely fluid state; when, if watched, it will be observed that, just upon cooling, a crust of solid metal will first suddenly form, through which the light of the internal red-hot mass appears of a beautiful brilliant green colour.

The non-metallic elements admit of ready division, as we have seen, dependent upon physical differences. The solid bodies of this division have been called 'metalloids;' and between these and the true metals the line of separation is not very definite.

For example:—Iodine, and also selenium, possess very strong metallic lustre, so that selenium has actually been classed with the metals, while silicon, as also tellurium, is now commonly associated with the 'metalloids.' The former commonly being produced as a dull brown powder; and the latter, although possessing lustre, being deficient in conducting power of heat and electricity.

The colour most prevailing in metals passes through all shades of white, of which the pure white of silver may be taken as the starting-point, and the blue white of lead the farthest remove from it; all others, with about five exceptions, being rangeable between these two shades.

Then follow the yellow metals; barium and strontium are pale yellow; calcium is deeper in colour; and gold of a rich yellow. Copper is the only red metal, for Deville and Wohler have found that titanium, which used to be classed with copper as red, is (when pure) steel grey.

The metals are nearly all destitute of odour or taste, but there are some exceptions to this. Thus peculiar odours will be evolved when we heat iron or copper; and one of our means of discriminating arsenic consists in the characteristic smell of garlic which is emitted when it is heated. The taste which is perceived in some, is no doubt due to some peculiar character, although, in some cases, it may depend upon voltaic action set up by the chemical agency of the saliva; the metal not being perfectly pure. This may be illustrated on a large scale by the well-known experiment of placing a piece of zinc on the tongue and a piece of silver under it, and then joining their edges, when a metallic taste will be perceived, dependent on slow solution of the zinc under electric action.

The three related qualities of malleability, ductility, and tenacity, differ much amongst them. A metal is said to be malleable when it admits freely of the extension of its surface in all directions, at the expense of the thickness, and does so without splitting out at the extending edges. Ductility signifies the capability of being drawn out into rods or wires, the granular particles of a metal thus elongating into fibres; and tenacity has some relation to the latter, and indeed to both qualities, for it means the power of resisting rupture upon the tension of a bar or rod, such as would be exercised in order to draw it into wire.

It might be imagined that the properties above described are so nearly allied, that they would be possessed in corresponding amount by any metal. But it is by no means so. Gold, for example, is the most perfectly malleable and ductile metal, for we may take a small button of gold and pass it over and over again between the rollers of a flatting-mill, and the drawing process would go on until stopped only by the imperfection of the rollers; but we might then continue by hammering, its malleability allowing of its being extended until even a grain would cover a circle of nearly nine inches in diameter. But gold, in tenacity, or the property needed for drawing it into wire, stands but seventh in the list of metals.

Again, iron, first in tenacity, stands ninth only in malleability; nickel, second in tenacity, is tenth in malleability; and palladium, third in tenacity, is, nevertheless, only tenth in ductility.

Crystalline metals never possess these properties. Thus bismuth may be broken up under even slight blows of a hammer; and antimony, or arsenic, may be powdered in a mortar. Again, brass, which has been drawn into wire, will frequently after a year or so become crystalline in texture, by slow change of molecular arrangement, when it will also be found to have become perfectly brittle. Also, by often annealing a bar of silver, or heating a bar of brass, the same molecular changes, and consequent brittleness, ensues.

The extent to which the drawing process may be carried in a truly ductile metal or alloy is only limited by the extreme tenacity to which the wire is brought, for at last the force of tenacity becomes so small from the small section of the metal that it is not equal to resist the disruptive force of the power required to draw it yet smaller.

The means employed for drawing wire is a severe test of the ductility and tenacity of a metal, which in the operation is forcibly pulled through a succession of holes, decreasing in size, and made in a hard steel plate. It is carried on upon a draw-bench (Fig. 1), which is a table fitted with a conical drum (A), revolved by machinery, or by a winch handle; this is sometimes furnished with a multiplying-wheel, for the purpose of equalising the somewhat intermittent motion liable to be produced when hand-drawing is employed, and this is further provided for by employing a fly-wheel also. The draw-plate itself (B) is a flat plate of steel, having a series of conical holes in it. The rod of metal is passed in at the larger opening on the one side, and drawn out by the smaller, which latter is carefully adjusted to the size of the wire required. As drawn it is wound by the drum from the reel (C). The plate-holes wear rather rapidly, especially in the case of drawing the harder metals, and so require constant attention to keep them to the guage, for which object, when they become enlarged, they are hammered up and re-pierced; but after a time the plate admits of this no longer, and has then to be renewed.

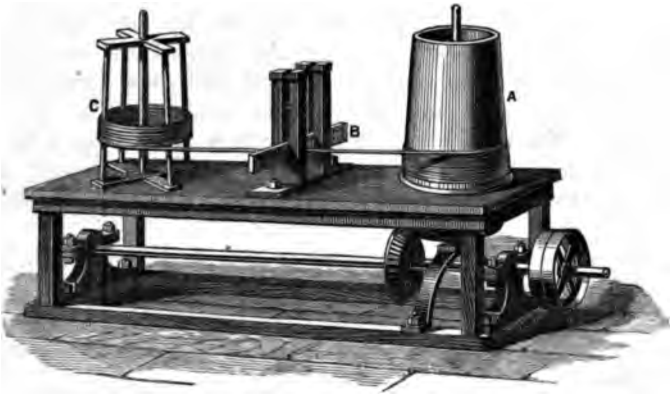


Fig. 1.

The workmen are often paid by the piece, and are then expected to deliver the wire of correct guage.

Occasional annealing is practised between the drawings, and as the heat used more or less oxidizes the surface of the metal, some liquid is generally employed to cleanse it; this also serves to lubricate the wire, and assist its passage through the plate. Many of the men have their own nostrums for this purpose, but sour beer is in very general use, and it is more effective when stale, as the slight acid present is all-sufficient to act upon the metal, and clean it.

Steel and iron wires are generally drawn red-hot, and passed forwards, and then back again through two holes in the plate, thus saving time, as well as too often reheating.

Of course it is requisite to employ the best qualities of metal, for only these would withstand the strain needed; and for alloys like brass, 'virgin metal' is used; that is, metal cast from fresh copper and zinc. It is cast in square bars, about 2 ft. long and 3 in. by ¾ in. section. They are first slit up into squares of about ¼ in. on each side by a circular saw. These soon draw to a circular section, and a good hand will draw them to an incredibly fine wire, and that without breaking. The wire is wound on the horizontal iron drum, which is of about 2 ft. in diameter, passing through the plate at a pretty quick speed, and the finer the wire the quicker the speed. It may range from about 80 to 300 or more feet per minute.

The author has two specimens of exceedingly fine wire in his possession. One in brass, drawn by a workman at the Kingston Companies' works at Birmingham, seven feet of which weigh only one troy grain. Some hundreds of feet of this were drawn in a continuous length for the Exhibition of 1862.

The other is a platinum wire, drawn by Dr. Wollaston's method, six feet three inches of which weigh one grain; so that taking the relative specific gravities of brass and of platinum into account, it will be seen that the latter wire is barely three times as fine as the brass, although drawn by the compound method to be described. Indeed the brass wire is infinitely finer than the finest hair.

Dr. Wollaston's method was to draw a platinum or gold wire as fine as he could, and then coat it with silver, to the extent of enlarging the diameter ten times. He then drew this compound wire down as before, and after this removed the silver by solution in nitric acid, thus leaving the platinum or gold untouched, although thus reduced in size. Iron wires may be drawn equally fine by similar means, but the silver here must be removed by amalgamation with mercury, wherein it will dissolve, leaving the iron intact.

The late Dr. Matthiesen showed the author an ingenious method for obtaining rough wires of metals difficult to draw in the ordinary way. He melted the metal in a tobacco-pipe, and then sucked it into the stem carefully. On cooling and breaking, a wire is found of the size of the stem-bore. *See* also Jour. Chem. Soc. for 1867, p. 202.

There are several conditions which may materially modify the properties of malleabity, ductility, and tenacity. The first is purity of a metal, and that to a very close degree, for a metal containing any notable amount of another one would be rather called an alloy. But mere traces of another metal often change a malleable, tenacious, or ductile one, destroying these properties to a greater or less extent. It has been stated that gold is the most malleable of metals. Now if a small trace of lead, itself a soft metal, be fused with it, the gold becomes as brittle as glass, and especially if the gold has any silver also with it. And this destruction of malleability and tenacity is yet more complete where antimony or some similar metals are mixed with the gold in very minute quantities.

In some bars, which in 1856 were referred to the author for examination between the Bank of England and the Mint, he found them containing mere traces of antimony and of tin together; and by these associates the tenacity was so completely destroyed that in passing the fillets of similar bars alloyed for coinage through the Mint draw-bench, as usual to equalise their thickness, they pulled to pieces with a fracture much such a piece of hard cheese would exhibit. This subject will be referred to when treating of the metal gold.

The great facility of drawing fine wires in brass, before mentioned, is quite hindered by a very small admixture of lead, and one to two per cent will quite spoil brass for wire-drawing purposes.

Next to purity comes the question of temperature, which exercises equal influence. Thus zinc remained for many years of little use in itself, its alloys being alone employed. At ordinary temperatures it was exceedingly hard and unmalleable; but it was then found that if heated somewhat above 200° Fahr. (= 94° Cent.) up to 250° Fahr. (or 121° Cent.), it became perfectly malleable, and capable of being rolled into very thin and uniform sheets, and thence it has come very largely into use. But if we carry up the temperature to 400° Fahr. = 205° Cent. it is again made quite brittle, so that it may be powdered by ordinary means.

Again, aluminium, magnesium, and some other metals may be drawn into wire only when heated, for at ordinary temperatures they are quite wanting in ductility. Brass, on the other hand, which is soft, tenacious, and ductile at ordinary temperatures, will be rendered quite brittle by heating to dull redness. But in this and many similar cases there is much alteration of molecular structure under the influence of heat.

Metals in general have their tenacity diminished by heating; there are exceptions to this however, as is the case with iron, steel, and gold. But they frequently have their ductility increased. The comparative tenacity of metals is determined by employing wires of exactly similar dimensions, and estimating the weight they will support without breaking; but care is requisite in the application of the strain of the weight, for if too gradually applied, a force insufficient to break the wire may in a ductile metal first so stretch it as to diminish the diameter to the degree at which a smaller weight than that required to rupture the original wire, will however effect it in its reduced diameter.

A malleable metal will by laminating have its character gradually destroyed, for its particles then become compressed and put into a constrained condition. But where this happens, annealing, by heating up and cooling slowly, will generally restore the original condition of particles, and render it again as malleable as before.

The following table shows the relative order of some of the more common metals, in which they possess the three qualities, taking them in the order of the numbers placed against each :—

Metals.	Malleability.	Ductility.	Tenacity.
Gold	1	1	6
Silver	2	2	5
Copper	3	5	3
Platinum	4	3	4
Palladium	5	6	7
Iron	6	4	1
Aluminium	7	9	2 ?
Tin	8	11	9
Zinc	9	10	8
Lead	10	12	11
Cadmium	11	7	10
Nickel	12	8	2 ?

A metal which may be cut cleanly through, or of which a strip on being bent exhibits no elasticity, would be called a soft metal. They vary much in hardness, but are not generally very hard when pure. As examples of difference in this property, mercury is fluid; potassium cuts like wax; lead is readily scratched, even by the finger-nail; gold is freely cut by an ordinary pair of scissors; while some few are even harder than steel. But the relative properties of hardness and softness are much controlled, even in the same metal, by change of temperature, and also by small traces of foreign matter. Iron-wire, for example, when pure, is very flexible and sectile; but iron associated with even one per cent of carbon, as in steel, is thereby rendered very hard and elastic.

The hardness of a metal may in most cases be increased by hammering, and thereby condensing the particles, also by heating and then suddenly cooling it; while, on the other hand, a hardened metal may be rendered softer by directly opposite treatment, viz. by heating and cooling down very gradually; this annealing action, as it is called, being in most cases slight separation of the metallic particles by heat.

A metal is said to be elastic when on flexion it readily recovers its previous form. Steel is most perfectly so; in lead the property is entirely absent. Alloying will often confer elasticity upon a non-elastic metal to a large extent.

All metals may be rendered fluid; but the degree of heat requisite for this varies very much. Thus, mercury fuses at 39° below zero, and hence is always fluid, at ordinary temperatures. Iron, on the other hand, is only fused at the highest heat of a good wind furnace, and some of the associate metals of platinum are scarcely fusible by the oxyhydrogen blow-pipe, or by voltaic electricity.

Table of Fusing Points of some principal Metals.

	Fahr. °		Cent. °		Fahr. °		Cent. °
Mercury	− 39	=	39·5	Zinc	773	=	412
Potassium	+ 144	=	62	Antimony	1150	=	621
Sodium	208	=	97·8	Silver	1873	=	1023
Tin	442	=	228	Copper	1996	=	1091
Cadmium	442	=	228	Gold	2016	=	1102
Bismuth	507	=	264	Cast-iron	2786	=	1530
Lead	617	=	325	Malleable-iron	undetermined		

The metals are the best conductors of heat amongst the solid bodies; but some transmit it much more readily than others. In comparing them, purity of the metal must be considered as it has much influence, and a small quantity of an alloying metal much diminishes the power of conduction. This fact may account for the differences in conducting power, shown between the numbers given by older experimenters and those of our own day. For example: Calvert and Johnson make silver the best conductor, and calling its power 1000, state gold to conduct with a power equal to 981; and then show how, by alloying the latter down to ·991, with silver, its conducting power is reduced to 840.

Order of Conduction in the Principal Metals.

1. Silver,
2. Gold,
3. Copper.
4. Aluminium,
5. Zinc,
6. Iron,
7. Tin,
8. Platinum,
9. Lead.

Metals conduct electricity, and this power is made extensively useful in the many thousand miles of metallic wires employed for the purpose of carrying electric currents over Europe and other quarters of the globe for telegraphic purposes. Davy, Becquerel, and others, have, at different times, estimated their power of conduction; and the late Dr. Matthiesen was actively experimenting upon the electric conductivity of metals. Amongst his results are the facts that impurity of a metal or alloying it greatly diminishes its conducting power. Rise of temperature again has the same effect. Thus between 32° F. and 212° or (0 C. and 100°) great diminution takes place, and that not uniformly, as some lose it much more in proportion than others, by thus raising the temperature. Many lose as much as twenty-five per cent of their conducting power at the lower degree.

If the connexion between the poles of a voltaic battery be made by a wire, the current, by this conduction, will pass freely; but if such wire be too small for the quantity of electricity which has to pass through it, the impediment thus offered will be evinced by the wire becoming red-hot. Hence, we have a means of determining roughly the relative conducting power of metals, by employing the same battery power upon small, equalized wires of each, and then observing how long a portion can thus be heated.

On the other hand, a wire may thus be made to indicate the quantity of electricity traversing a battery by the length the battery will be capable of rendering incandescent. A striking way of showing the difference between two metals in this power consists in making a compound wire of some six inches long, composed of alternate short lengths of platinum and silver; this, with a properly proportioned battery power, will show, while the current is passing, alternate red-hot platinum links, with cool silver ones; the platinum being the worse conductor, offers such a check to the free passage of the electric current that it becomes red hot, while the good conducting power of the silver allows of its free transmission. Matthiesen also shows that the conducting power is greatly altered in hard drawn wires of pure metals, when the same are annealed.

Order of Electrical Conducting Power.

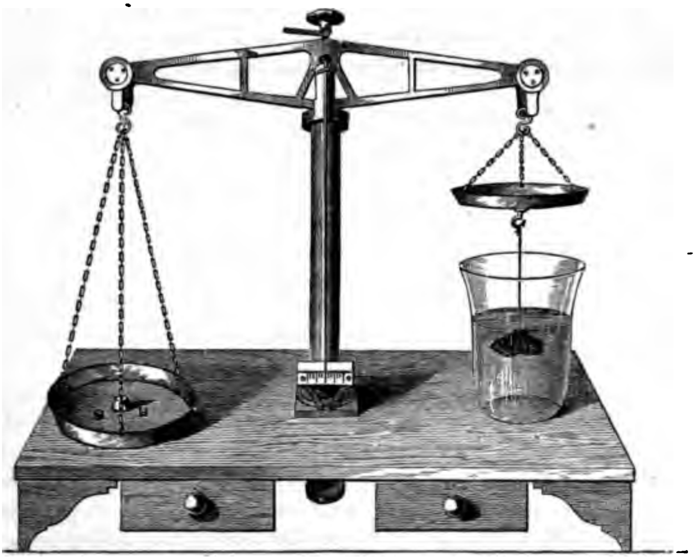
1. Silver = 1000
2. Copper = 999
3. Gold = 777
4. Zinc = 290
5. Platinum = 180
6. Iron = 168
7. Tin = 123
8. Lead = 83
9. Bismuth = 12

The term 'specific gravity' is synonymous with density, and the densest bodies in nature are found amongst the class Metals; and inasmuch as they differ very much amongst themselves in density, we may often identify a metal by ascertaining its specific gravity. For example, tin, silver, and platinum, are each white metals, and thus in external appearance resemble each other very closely. But tin has a gravity of 7·292, silver of 10·53, and platinum of 21·53, hence the specific gravity would at once to a certain extent distinguish between the three.

The specific gravity of a body may be defined to be the weight of an accurate bulk of such body as compared with the same bulk of another; the latter being some fit one chosen as a standard to which all other solids and fluids are so compared. For this purpose pure water is employed, and of a fixed temperature, viz., 60° Fahr. (= 15·5° Cent.). Water has been adopted for the following reasons: first, it is always to be had; secondly, it is uniform in composition; and, lastly, possesses certain available qualities which will be seen to be essential. Water then is called unity, or 1·000.

Now, suppose we have a fragment of metal, and desire to know its specific gravity, the following is the proceeding: first, weigh the mass accurately in a delicate balance, and note the weight; next place under the same arm of the balance a glass of distilled water at 60° temperature; and from a small hook, which is generally placed below the short hung pan, furnished to balances adapted to this operation, hang the metal by a fine horsehair, and allowing it to dip below the surface of the water, so as to be completely immersed; again weigh. It will now be found to weigh less than in air, and the difference between the two weighings will be exactly the weight of the bulk of water displaced by the solid; in fact, we have accomplished the apparently impossible task of weighing a bulk of water mathematically equal to the bulk of the irregularly shaped piece of metal. Care must be taken that no air-bubbles are adherent to the specimen or to its suspend-

Fig. 2.



ing hair which would of course give it a false buoyancy in the water.

Now having obtained these two terms, viz., the weight of the metal and the weight of an equal bulk of water, it only remains to work out a question of proportion thus stated. As the weight of the bulk of water is to the specific gravity of water, so is the weight of the metal to its specific gravity. And, further, as the middle term here is unity, it simplifies the question into dividing the weight of the metal by the weight of water.

But giving an example will at once render this plain. Having a small fragment of metal to operate on, I weigh it, and find its weight is 92·71 grains; then on suspending it in water, its weight is reduced to 80·01 grains; thus the loss, or 12·7 grains, is the weight of the water displaced. Then the following calculation gives the specific gravity required —

	Weight of Water.		Sp. Grav. of Water.		Weight of Metal.		Sp. Grav. Required.
As	12·7	:	1·000	::	92·71	:	7·3

But it is frequently required to obtain the specific gravity of bodies, which being in fragments, we are unable thus to suspend to the pan of a balance, but we may in such a case get the same data by employing a specific-gravity bottle, such as is commonly used for fluids; where, of course, accurate comparative bulks are easily obtained by filling such a bottle, and weighing, thus doing away with the need of any calculation. Now as the bottles ordinarily sold are often not very well constructed for their purpose, I will describe a good form; when the reader may notice one or two points upon which their efficiency much depends.

A bottle is blown of glass, and for the purpose of experiments on solids it should not be too thin, for a balance may be employed in these cases capable of carrying some 2000 grains in each pan. It is best of a pear shape, and may be made to contain any quantity, as, for example, 250, 500, or 1000 grains, but the latter is the capacity most suitable to our purpose. Its neck should be large, viz., of about half an inch internal diameter, and fitted with a stopper formed out of a piece of capillary tube, the upper and lower ends of this stopper being cupped out as in the drawing; the lower cup prevents any air being retained between the upper surface of the water and the stopper,* which is apt to be the case when it is not so hollowed. The upper cup retains any of the water which may escape by expansion; for as the complete fulness of the bottle is ensured by putting in the stopper when the water is quite at the top of the neck, the excess is squeezed out on stoppering, and so overflowing, the outside of the bottle requires careful wiping, during which operation the temperature will in all probability be raised. Here then, the upper cup comes into use to retain the fluid forced out by this expansion.

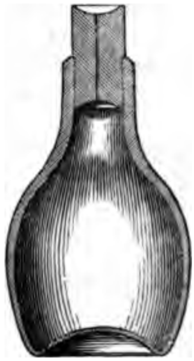


Fig. 3.

The adjustment is performed by the maker, who grinds in the stopper to a point where, at a given temperature, exactly 1000 grains will be contained. But as this is an operation requiring much care and time, it should always be verified before first using it. Lastly, it should be supplied with a counterpoise weight, corresponding exactly to the weight of the bottle, plus 1000 grains of distilled water, or such other weight as it has been made to contain.

Now to take an example of the application of such a bottle to our purpose, let us suppose it is desired to obtain the specific gravity of a form of silver amalgam, which is in loose grains. The bottle is first filled with water (previously brought as near as possible to 60° Fahr.), the temperature is then accurately adjusted by putting in a fine cylinder thermometer and stirring the fluid with its stem (an operation easy of performance from the width of the neck of the bottle), till correct, then, after warming up by a vessel of hot water, or cooling down as may be needful, the stopper is put in so as to retain its exact quantity of water.

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* The bottle is represented as not quite full, in order to made plainer the shape of the stopper.

Next, a carefully weighed portion of the amalgam is put into the bottle, and the stopper again inserted; after which the overflow water, caused by this introduction, is quickly and well wiped off. It then has to be weighed against its counterpoise, having first verified its temperature, and it will of course be found that weights have to be added beyond the counterpoise, but less than the weight of metal put in, by just the weight of water displaced from it.

The difference between the present added weight, and the previous one of the amalgam, will of course give the weight of the bulk of water, equivalent to that of the body under examination. Lastly, the remaining steps of the operation are precisely the same as in the one first described.

In both of the operations detailed it is necessary to employ a balance, but this instrument may be dispensed with, by the employment of the gravimeter for the purpose of obtaining these weighings.

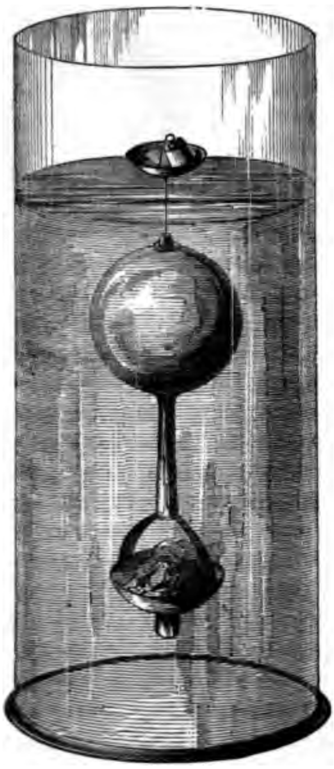

Fig. 4.

The gravimeter (a modification of Nicholson's hydrometer) consists essentially of a hollow ball capable of floating in water, and furnished with a lower and upper stem, the latter being formed of a slender wire having a zero-line marked upon it. If made as free as possible from sources of error, it should be of a bulk which, immersed in water at 60° up to this stem-line, would displace exactly 1000 grains of that fluid; while the actual weight of the instrument should be 700 grains, consequently, to sink it in water to the stem-mark, it would be requisite to put weights amounting to 300 grains into the upper dish. It is evident, then, that we have here the means of actually weighing any substance amounting to not more than 300 grains in weight, by putting it into the upper dish, and adding weights till the instrument is brought down to its zero-mark, when, by deducting their amount from the 300 grains requisite so to sink it, the weight of the solid is obtained.

But let us work out the first example given by means of the gravimeter. Suppose the portion of metal mentioned at page 20 be taken: let it be placed in the upper dish, and the instrument then be floated in a capacious glass vessel of distilled water at 60° Fahr., as shown in the drawing. It will then be found that, in order to sink the gravimeter to zero, weights to the amount of 207·29 grains must be added. Now this, deducted from 300 = 92·71, the weight found before by the balance. The mass of metal is then removed, placed in the lower dish, and the instrument immersed as before, when a second addition of weights will be required, viz. of 12·7 grains: this, then, is the weight of water displaced. And, lastly, having obtained these terms, it only remains to calculate the result, as in the former operation.

In using this instrument, again it is necessary to be very careful that no air-bubbles adhere to any part of it under water, as they are rather apt to do. The larger weights used should be dish-shaped.

The temperature 60° Fahr. (= 15°·5 Cent.) is now almost universally employed as the standard temperature at which all specific gravity should be taken; and when it is remembered that all bodies expand by heat, and that in greater proportion as their density decreases, it will be evident that much care is required to ensure accuracy in the temperature of the water, as a given bulk will weigh considerably less if we raise its temperature even but a few degrees.

The metals have been divided, dependent on their specific gravities, into two classes, viz. heavy and light. Those have been designated heavy which have specific gravities ranging from 5·3 to 21·5: while, on the other hand, the specific gravities of those ranging from 0·593 to 5·0 have given them the title of light metals.

The specific gravities of the principal metals are here given, but it must be remembered that these are subject to variation, dependent upon the mechanical condition of the metal; and as an extreme example of the effect of molecular condition may be given Dr. Wollaston's estimates of platinum under its various stages of manufacture:—

Cake Platinum, when from the press . . .	10·0 S. G.
Platinum after contraction by heat, but before forging	17·0 to 17·7
After forging, when ready for manufacture .	21·25
After drawing into wire	21·53

Specific Gravities of some of the Principal Metals.

Platinum . .	21·53	Nickel	8·82
Gold . . .	19·34	Iron	7·844
Mercury . . .	13·59	Tin	7·292
Palladium . .	11·80	Zinc	7·146
Lead . . .	11·35	Antimony . .	6·71
Silver . . .	10·53	Aluminium . .	2·60
Bismuth . . .	9·80	Magnesium . .	1·743
Copper . . .	8·93	Sodium . . .	0·972
Cadmium . .	8·69	Potassium . .	0·865
Cobalt . . .	8·95	Lithium . .	0·593

It has just now been stated that some clue may often be obtained to the composition of an alloy by taking its specific gravity; and although, in many cases, mixtures of metals of different densities may give a mean specific gravity varying just in proportion as the lighter or heavier component predominates, yet the law does not universally hold good; for, in some cases, where we fuse metals together, we get expansion of the alloy, and in others contraction.

In the first case, therefore, the specific gravity shown would be lower than the true one, while in the latter a greater specific gravity than correct would be indicated.

In such cases, of course, the specific gravity would mislead as to true composition; but there are many where we may make use of it as an approximation to composition: as, for example, in mixtures of gold and silver, or gold, silver, and copper,—the usual constituents of gold coin and plate. Suppose such a mixture be examined, and the specific gravity found to be about 18·5: with the previous knowledge that standard gold consists of 22 parts of pure gold combined with 2 parts of alloy, and, further, that the specific gravities of gold, silver, and copper are 19·34, 10·53, and 8·93 respectively, we should, by a simple calculation, discover that the alloy was standard gold: or, similarly, if it was found to be only about 16·8, we should know that it was 18-carat gold; that is, gold containing 18 parts of pure gold, with 6 parts of alloy. But, of course, such estimates can only be used as mere approximations to composition, and must be taken in connexion with other physical appearances influencing the judgment of the operator in such cases.

We may, in conclusion, take the case of gold associated with quartz, as it usually is in the mine. Here, as quartz has a specific gravity of not more than 2·6 to 3·0, while gold has that of 19·34, a fair rough estimate may be made of the amount of gold contained in any such sample by the specific gravity it gives.*

It must be clearly understood, however, that in calculating the specific gravity of a mixture of two metals, we must not calculate from the relative proportional weight of each component, but from the relative volumes of each. Matthiesen† has shown this, and gives a very marked example in proof of it, choosing for illustration an alloy of equal parts of platinum and of aluminium, as being widely separated in their specific gravities. Calculating the specific gravity from the mean of equal quantities of the two, taking platinum at 21·53, and aluminium at 2·6, we should assume that of the alloy to be 12·06. But as 1 part of platinum displaces 0·047 of water, and 1 part of aluminium 0·4 of the same, and assuming that no expansion or contraction takes place in alloying the two, 'we may look on such an alloy, when taking its specific gravity, as if the two metals were hung side by side in the water. If, therefore, the theoretical specific gravity of the alloy be required, it will be the weight of the two metals divided by the quantity of water displaced by them, or $\frac{2}{0{\cdot}4+0{\cdot}047} = 4{\cdot}46$, the true specific gravity.' Actually 4·474.

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* Phillips' *Mining and Metallurgy of Gold and Silver*, p. 236, gives a table showing the proportionate weight of gold in a mass of auriferous quartz of known specific gravity.

† *Quarterly Journal of the Chemical Society*, vol. xv. p. 106.

The metals are found in nature often in the metallic state, but more frequently in combination with some simple non-metallic element, or in the more complex condition of salts. Of native metals, the chief are the noble, their low affinities for oxygen, &c. rendering them more free thus to exist in the metallic condition. But these are always associated with certain others of the same class: thus, silver is never found free from gold, although often in very small quantity or proportion; then gold has always more or less silver with it. Again, native gold often contains platinum, with some of its associate metals; while platinum itself is always alloyed with palladium and the other 'platinum metals.'

The class of base metals, from their powerful affinity for non-metallic elements, are nearly always combined with one of the latter, and more commonly with oxygen or sulphur; less frequently with chlorine, and still less with iodine or bromine. And, lastly, some of this class are found as salts; as silicates, carbonates, sulphates, phosphates, &c.

Among the noble metals, however, mercury and also silver are very largely found, in combination with sulphur; then, on the other hand, some ores of base metals—as galena, for example—are found containing silver, and with the latter traces also of gold.

Deposits of metallic ores are always found in certain geological positions only, and are not distributed indiscriminately upon the earth's surface: hence, if we know the geological character of a district, we may generally safely pronounce upon the presence or absence of particular metallic deposits.

Metallic deposits are found generally in the localities of granite rocks, and those of porphyry and clay-slate, and the older igneous ones, but most abundantly in sedimentary rocks, or in places where these two classes come together.

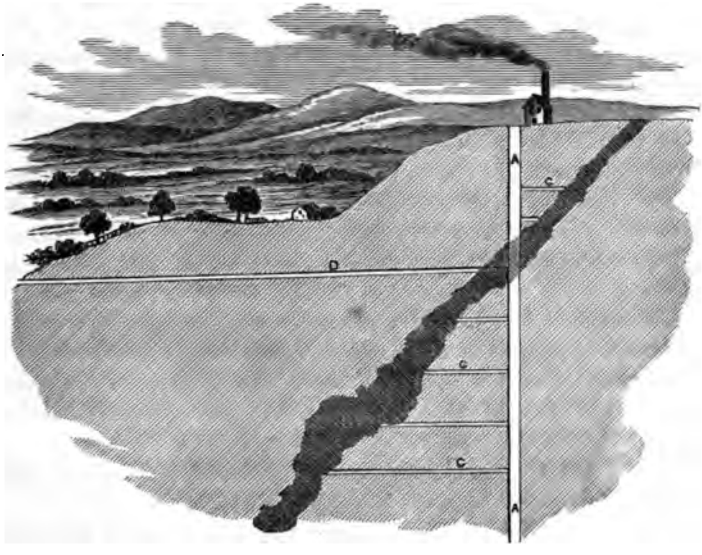

Fig. 5.

The cavities wherein metals are found are termed mines. These may be either surface excavations, as in some of the shallow gold diggings or stream tin mines; or they may be deep cavities, extending often to so great depths as to require extensive mechanical arrangements for drawing the ores to the surface, and also for freeing the workings from the influx of water, which, if not constantly removed, would collect in such quantity as put to a stop to all mining operations. Sometimes the deep excavations may be so made into hills that the water is readily carried away into the adjacent valleys by what are termed adit levels (D fig. 5), these levels or drains being in such situations, even of some miles in length, whereby the water may be carried quite clear of the workings so as to flow away. But when a mine is carried much below the level of adjacent valleys the water is then pumped up by machinery, and delivered into the nearest adit level, having been previously collected in a hole situated in the lowest part of the shaft, and termed the 'sump.'

Metallic ores are commonly found in veins or lodes, these traverse the earth's depths, passing down at more or less inclination to its surface. They occasionally open out into large cavities full of rich ore, these are termed by the miners 'bunches.' In these veins the ore is always associated with stony matters called gangue or vein-stone. Copper, lead, zinc, silver, and sometimes gold and some others, are thus found. Some ores lie in beds, as iron-stone for example, and these beds of ore are often interposed between other layers of more or less value.

In the case of our iron-stone the adjacent beds are composed of coal, and also of limestone; both indispensable materials in the smelting of the ore itself.

Some ores are found as fragmentary deposits associated with sand or gravel, or like materials, which with the metal has been washed down from the mountainous districts and thus deposited in valleys or the beds of streams. In these the metallic matters are pretty much collected together, assisted in this by their greater specific gravity bringing them to rest before the lighter sand or stony matters. Gold and tin are thus found; and bog-iron ore may be classed with these fragmentary ores.

A tolerably correct judgment having been formed as to the presence, situation, and direction of a lode of ore, the first step for realising it is to sink a perpendicular main shaft (A fig. 5) to the depth necessary to enter the lode, which entry is generally calculated for at about forty fathoms depth. The ore is then followed by carrying out galleries (B fig. 6) right and left in the direction of its 'strike,' and these are worked for it until the extremity of the lode is reached. But as the lode 'dips,' or takes an angular direction crossed by the perpendicular shaft sunk, cross-cuts (C fig. 5) are made at about every ten fathoms, both above and also below the first working point. The cross-cuts being carried forward into the lode, when galleries are again carried right and left, as before, at right angles to these cross-cuts.

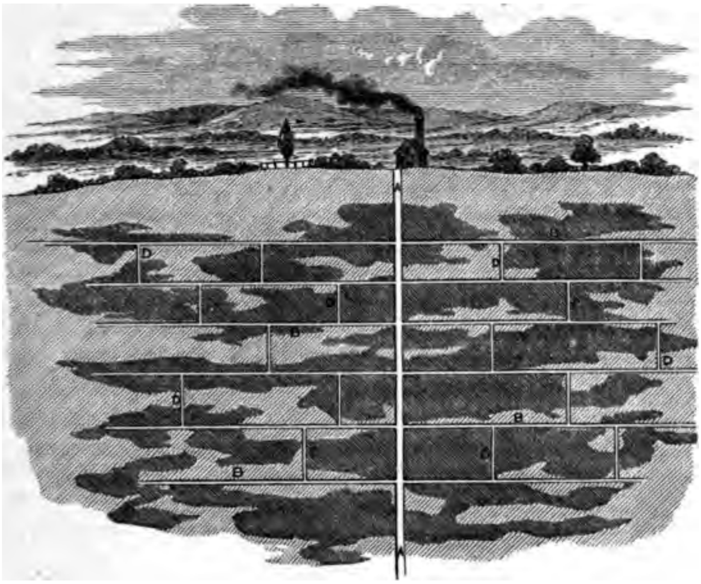

Fig. 6.

But as these workings extend it becomes needful to have more connecting cuts, not only to facilitate the working and removal of the ore, but also to assist in ventilation, which becomes defective just in proportion as the works increase in extent. Therefore a fresh set of perpendicular openings are formed connecting the galleries of different levels. These winzes, as they are termed (D fig. 6), are sometimes sunk down from an upper to a lower gallery, or they may be driven upwards from a lower to an upper through the substance of the lode.

Such is in brief the working of a mine in its early and simple condition; but, of course, in time, as the workings become more and more extensive, additional shafts become necessary, together with increased means of draining and ventilation; improvement in the latter becoming imperative by the blasting operations, which further tend largely to vitiate the air, for although the miner detaches the ore chiefly by means of his pick, or by a hammer and wedges, he also, for detaching larger masses, employs gunpowder or gun-cotton, and by thus blasting at proper points can much facilitate his operations.

The large cavities formed by the constant removal of the ore, are kept open by erecting strong timber supports, which become absolutely needful to prevent collapse and falling in of the galleries.

The detached and broken-up ore is removed to the main shaft in trucks or barrows, and thence to the surface in large iron buckets called 'kibbles,' the raising rope or chain being wound upon a drum or 'whim' by machinery placed at the shaft mouth for the purpose.

The depth of some mines is very great, thus some of the Mexican silver mines are sunk to near 350 fathoms, and consequently with very large shafts, that of the Rayas mine is full 30 feet diameter at its outlet.

In Cornwall some of the mines have their shafts passing down close to the range of the cliffs, to a depth of about 250 fathoms, and the ore taking a seaward direction, the galleries pass actually under the sea-bed for long distances; their roofs being formed of rocks and sometimes dipping so close to these galleries as to leave so thin roofs, that at times the sound of the sea above is audible to those in the workings.

On taking a mass of any ordinary ore in the hand it will be seen to be more or less mixed up with gangue in the form of earthy matters, quartz, &c., the latter or some analogous material constituting the vein-stone of the mine. Hence before smelting, some operations are needed in order as much as possible to get rid of bodies which would occasion hindrance and often loss to the smelter. The first and most obvious plan is that of hand-sorting, which is done at the time by boys and often by young women, much quartzose matter is at once rejected, large lumps broken up by hammers, and again the richer parts separated from vein-stone; while any portion of the latter showing the least indication of metallic contents is set aside for further mechanical treatment.

The mechanical operations used are crushing, stamping, washing, &c. For as metallic ores generally have a much higher specific gravity than the quartz or earthy matters, the latter may, by washing after crushing, be readily separated from the former.

Crushing is usually effected by a roller machine where the ore is dropped from hoppers first between two revolving cylinders, similar to those shown in the article upon gold. The drawn-in ore is crushed in passing through, and is often received below by a second or even a third pair of rollers placed under the first, and with the cylinders set closer, so as further to reduce the size of the crushed ore. The stamping operation is effected by placing the ore in a kind of mortar formed of iron, and in which a heavy iron stamp works (see also chapter upon gold). A series of these mortars and stamps are generally placed side by side, so as to be worked by the same revolving axis, the latter having a series of cams round its circumference, each of which engages a tongue projecting from the stamp arm, and so raises it, allowing it to fall on the passing round of the cam, motion being given to the cylinder by a water-wheel or other convenient power. The plan adopted, however, for crushing or stamping is varied according to the nature of the ore and its associations.

Washing is either performed in the jigging machine, or upon the buddle, or inclined trough. In the first the material is placed in a large square frame having a sieve-like bottom; this is raised up and down in a tank of water, and at the same time a peculiar motion is given to it so as to separate the broken ore and allow of the finer parts passing through the sieve, while the coarser remain in it, with the finer and lighter earthy portions above all. But the latter, as it contains much valuable ore in a very finely divided state, is ground further, and converted into a slime or metallic mud with water, and sufficiently thin to allow of the heavier rich particles, subsiding to the bottom of settling pits into which it is passed for this end.

Sometimes the jigging is effected by a stream of water passing through fixed sieves.

The buddle is a plain trough through (or over) which a thin sheet of water is kept flowing. It is generally about 10 feet long by 3 wide, and the powdered ore is spread in the upper part so as to be carried gently down the trough by the flow of water Thus the richer parts of the ore come to rest before washing off the inclined trough, and are collected from time to time.

For washing crushed gold quartz such a trough is covered by a blanket, in order more surely to retain the valuable metal.

In all these cases the earthy parts wash off and are retained as 'slimes' for after treatment.

Sometimes a metallic ore is almost masked by others of a different nature so as to constitute but a small portion of the whole matter to be operated upon. Thus copper pyrites in addition to copper sulphide, contains iron and also arsenic sulphides. Nickel ore is again largely associated with arsenic. In such cases roasting is employed with exposure to air; this expels volatile matters, and effects oxidation of some others. Thus in copper pyrites, volatile matters as arsenic are first separated, while the iron is oxidized in such a manner as to render it readily separable from the copper. Similarly arsenic is volatilized from nickel ore by roasting.

At times the ore of the sought metal exists only in incredibly small proportion in the mixed mass. Thus Mexican silver ores in some cases contain not more than two-tenths per cent of silver, and yet are profitably worked for the latter metal. In such cases, bodies are employed in the course of the operation which have very strong affinity for the metal sought, as mercury, for example, in these Mexican silvers, as also in gold quartz.

In such cases the mercury forms a heavy analgam with the precious metal, having dissolved it completely and so separated it, and thus admitting of the other and lighter earthy matters being safely washed away from the amalgam which is left.

CHAPTER II.

COMBINATIONS OF METALS WITH THE NON-METALLIC ELEMENTS.

MECHANICAL union between the similar particles of any body, a piece of iron for instance, is kept up by the force of cohesion, a powerful force acting at sensible distances; that is to say, that although such a piece of iron is held together with a power requiring a large expenditure of force for its rupture, yet there are actually interspaces between its particles; in fact it is porous.

And similar powerful cohesion takes place between the particles of dissimilar bodies having like natures, as, for example, between copper and tin in the formation of bronze, but between all such the union is comparatively feeble, and purely mechanical, and, moreover, the resulting compound body partakes of the characters of its constituents just as one or other is in excess.

But chemical union is of a very different and more intimate nature, and is exercised in the strongest degree between bodies which differ most widely in properties, so that on close approximation of the particles of two bodies having chemical affinity for each other, this force comes into play, and by union we have a new body wherein none of the characters of the components are traceable.

If a portion of tin held together by its own cohesion be immersed in the fluid mercury, simple affinity will cause the tin to break up and dissolve, rendering the mercury more or less dense and viscid just in proportion to the amount of tin dissolved by it. But if we distil the mixture the mercury will all distil off, and the metals thus again separate into mercury and tin.

If, however, in place of mercury we employ hydrochloric acid as a solvent, true chemical affinity comes into play, and the tin breaking up the acid into its constituents, displaces the hydrogen of the acid and unites with the chlorine, and we get a salt of tin as the result, in fact, a totally new and true chemical compound.

Affinity, then, appears to be of two kinds; first, that simple action whereby bodies have a tendency to unite or to dissolve one in the other, but without actual change of characters, whence we get a resulting compound having a composition and properties, the mean of those of its constituents, such, for instance, as we see in the union of metals with each other in the formation of alloys. And, secondly, the more complex action whereby new compounds are produced, as where metals combine with non-metallic elements and give rise to bodies wherein the chemical and physical characters of their constituents are lost.

Both these may be exercised with various amounts of energy. Thus, for the first, we may mix zinc and copper in almost any proportions, and the result will be a tolerably intimate alloy; but if we attempt in the same way to mix zinc with lead, we shall succeed in uniting only a very small proportion of zinc with the lead (less than two per cent). In fact, the zinc and lead have not the amount of affinity for each other that the zinc and copper have.

And no less similar variety is found in the degrees of chemical affinity. In truth, it is on these degrees that all our operations of analysis for the discrimination and estimation of unknown bodies depend.

For example.—The tendency to solution and elementary union appears equally strong between nitric acid and either a piece of copper or of iron. If we dissolve a piece of copper in this acid, true chemical affinity produces a new body, a salt of copper; and on evaporating such a solution, we crystallize out a blue salt, in which none of the physical characters, either of the acid or metal, are discernible. Now, if we again dissolve some of these crystals in water, and put a plate of iron into the solution, we shall get the iron dissolved, and metallic copper again separated; for the iron and acid have greater affinity for each other than the copper and acid have; and hence the acid now unites with the iron, setting the copper free.

Chemical combination is very commonly effected by such displacement. Thus, in the case before mentioned of solution of tin in hydrochloric acid, the combination takes place by the simple displacement of the hydrogen of the acid by the metal, and in that of iron in the copper solution, the same removal occurs, all other things remaining the same.

But there are cases where direct chemical union is effected, as where we put a metal into chlorine gas, or heat a metal with sulphur; in all which cases direct union takes place, with the formation of new and true chemical compounds. As has been remarked, where simple affinity is exercised the bodies may mix in any arbitrary proportions. But the case is altogether different where chemical affinity results. For all true chemical compounds are formed only in certain definite proportions, the combining quantity being always fixed, and the same for the same element.

Thus, if we add potassic hydrate to cupric nitrate in solution, we shall find that for every 295·5 parts of crystals employed, we should, after boiling and heating the precipitate, find it amount to exactly 79·5 parts of cupric oxide; and for the exact precipitation of it just 112·2 parts of potassic hydrate would be requisite. Again, if we heat this cupric oxide in a glass tube, and then pass a current of dry hydrogen gas over it, we should get 63·5 parts of copper and 18 parts of water; the latter resulting from union of 16 parts of oxygen separated, with 2 parts of the hydrogen employed, and no matter how obtained cupric nitrate would always be composed of its elements in mathematically the same relative proportions.

Again, in the removal of copper from the same solution, by means of iron, for every 63·5 parts of copper so separated 56 parts of iron would be dissolved.

Such numbers used to be called the equivalent numbers of these elements and compounds, but now the term atomic weight is used.

We learn, then, that bodies combine chemically only in their atomic weights, or multiples of them. Secondly, that all chemical compounds are perfectly definite in their nature and constitution, and the ratio of their elements is constant.

Thirdly, that the combining quantity of a compound is the Sum same of the combining quantities of its constituents.

The metals have generally a very strong tendency for union with the non-metallic elements, and so form binary compounds with them, a simple body thus combining with a simple one. The classes of oxides, chlorides, sulphides, &c., are produced in this way; and of these the first class, viz. the oxides, forms the most considerable and important one.

Metals with Oxygen.—Some metals by heating, with free exposure to air, at once lose their metallic character, and assume that of an earthy-looking mass; such was called, in old times, the 'calx' of a metal, whence arose the term calcination; the change effected by the operation being really oxidation, by combination of the metal with oxygen abstracted from the air.

Their affinity for oxygen varies much in amount; in some it is so powerful, that they can only be preserved in the metallic state by immersion in a menstruum which contains no oxygen, or else by sealing them in glass tubes with as little air as possible, simple contact with air sufficing to oxidize them. Thus potassium and sodium are kept in mineral naphtha, a body composed of hydrogen and carbon only, and yet, even under these favourable conditions, their surface will slowly oxidize.

A striking illustration of their affinity for oxygen is afforded by throwing some potassium upon the surface of a basin of water. It immediately robs the water, upon which it rests, of oxygen; and so great is the heat attending combination, that the hydrogen set free is inflamed, and burns with a flame-coloured violet by the metal, a portion of which is volatilized by the heat generated.

A second class will be slowly and quietly oxidized by exposure to air, especially if it contain the least trace of moisture; but, in these cases, the action is, of course, superficial, and hence the newly-formed oxide will act as a protection to the metal below it, by preventing subsequent free action of the air.

Thus lead or iron becomes superficially rusted or tarnished, and this surface oxide removed, the same action would again be carried on. Many of these oxidize very readily upon fusion, and from such the separation of oxygen is a task of some difficulty. Thus lead may be entirely converted into oxide; and zinc, when heated somewhat above its fusing point, will manifest the intensity of combination by actual combustion, the oxide being thrown off as white fumes. Some metals are thus combustible; and, indeed, in most cases, their combustion merely depends upon sufficiently powerful means being employed to effect it. For we may burn iron in very considerable mass, if we first heat it, and then throw a jet of oxygen gas upon it. Thus the whole will be converted into oxide.

There is yet a class of metals which cannot be made to combine directly with oxygen, and, moreover, whose oxides, when obtained by secondary means, may have their oxygen easily separated by heat alone.

Many metallic oxides are found in nature, and constitute principal ores of their respective metals. Thus the hematites, specular iron, and magnetic oxide, are all of them oxides, and yield the best varieties of iron. Tin is reduced from its oxide; and manganese, chromium, and several others exist largely in nature in condition of oxides.

There are four methods of artificially forming them. First. The heating of a metal, in air or in oxygen gas, suffices to convert it into an oxide, and, in this way, some oxides so formed may be converted into others of higher grades. But this plan is chiefly applicable to form oxides which are fusible or volatile. The ordinary red lead of commerce is so formed; lead is first heated, without allowing it to fuse; thus a protoxide is produced. This is then exposed to a temperature of 600° F. = 315°·5 C., a current of air being at the same time thrown upon its surface, whereby an additional quantity of oxygen is absorbed, under the influence of the slight increase of temperature, which changes the whole into the beautiful red pigment.

Second. If we heat the nitrate or carbonate of a metal to redness, the acid will be evolved and the oxide left. By thus exposing the white carbonate of lead to heat, its colour soon changes to a lemon yellow; and, on examination, it would be found to have been deprived of its acid, and a protoxide left.

Again, the best method of forming cupric oxide consists in acting upon copper by nitric acid, and so obtaining a nitrate; then, by drying and heating to redness, the oxide will remain. In this case, the metal is oxidized by decomposition of some of the acid in forming the nitrate, and the subsequent isolation of the oxide is simply (as before remarked) caused by the evolution of the acid of the salt, under the influence of the heat to which it is exposed.

In the case of some metals so acted upon by nitric acid, we do not get the subsequent formation of a salt carried on, but the oxide so formed remains suspended as a powder in the undecomposed acid. Such a result depends really upon the newly formed oxide having acid properties. Hence, by means of nitric acid, some metals, as tin and antimony, may be converted into acids.

In some cases, if we deflagrate a metal with a body rich in oxygen, as potassic chlorate, or potassic nitrate, or a metallic sulphide, with nitre, we obtain its oxide. Thirdly, if we ignite the sulphates of some metals we obtain their oxides. Thus on heating the double sulphate of alumina and ammonia we drive off all but the aluminium oxide. Again, the bodies known in the arts as rouge, crocus, colcothar, &c., are oxides of iron obtained by thoroughly igniting the ferrous sulphate.

Fourthly, we get metallic oxides, but in the hydrated state, by adding an alkali to a solution of a metallic salt in water. Thus, if zincic sulphate or cupric sulphate be treated with caustic potash, double decomposition takes place, and bulky hydrated oxides fall. From these the water may generally be expelled by heat, although, in some cases, with difficulty. In others, it will be driven off at the temperature of boiling water, or even under that. Thus cupric oxide is precipitated as a green flocculent hydrate by potash; but the mere boiling of the precipitate suffices to dehydrate it, rendering it black and pulverulent.

Lastly, some metals are oxidized by alkalis. Thus, if metallic zinc or aluminium are heated in strong caustic potassa, water is decomposed, its hydrogen evolved; while its oxygen oxidizes the metal. The latter then dissolves in the potassa solution.

When we speak of reducing a metallic oxide, we commonly mean the separation of the oxygen, and the restoration of the metal to a reguline state. But the term is also used when we describe but a partial separation. Thus we speak of reducing peroxide of iron to the state of protoxide, and the like.

Reduction is effected, in the case of the noble metals, by the simple application of heat. Thus, heating oxide of gold, or silver, or platinum, to a very moderate degree, will leave a clean, brilliant mass of the metal.

Next, there exists a class rather more difficult to reduce, which, in addition to heat, requires some body to be employed which, by its affinity for oxygen, shall assist in its abstraction. Thus the formation of oxide of lead was just now spoken of, by means of heating the carbonate. Now, if we continued the heat, all we should effect by it would be, either the fusion of the oxide, or else its conversion into an oxide of higher degree. But if a small quantity of charcoal (or carbon) be added, the latter will at once abstract the oxygen for its own conversion into carbonic acid, and metallic lead will be set free.

In such cases, where a high temperature is employed, carbonic oxide is evolved. But if the temperature be only moderate, carbonic acid is given off.

Gay Lussac says that carbonic acid in these cases of reduction becomes carbonic oxide by taking another atom of carbon. The latter gas then coming in contact with the metallic oxide is reconverted into carbonic acid again; and these changes are thus repeated until the whole of the metallic oxide is reduced; the actual agent of the reduction being carbonic oxide.

On the large scale, this operation is generally performed in a refractory clay crucible, which is filled with a mixture composed of the oxide to be reduced, and charcoal powder. Sometimes, instead of forming such a mixture the oxide is put by itself into a crucible which has previously been thickly lined with a coating of charcoal, which latter furnishes the carbon as the operation proceeds.

An essential addition, in these cases, is that of a body termed a flux (a little borax, for example) which is strewed over the surface of the mixture before the operation is commenced. This enters into fusion before the reduction begins; and as soon as it does commence, and small grains of metal are set free, they are surrounded and kept clean by this flux, and so enabled to flow together in a compact button or mass. This is aided by the evolution of gas formed, which keeps up a constant circulation, assisting the clean globules to come together, their union being finally completely brought about by a few gentle taps of the crucible on removing it from the fire. Metals so reduced generally contain traces of carbon, and even of boron from the borax used.

A class of oxides, to which the foregoing treatment is not applicable, may be very elegantly reduced by placing them in a glass tube, heating it red hot, and then passing a current of quite dry hydrogen gas over them. A large two-necked bottle is fitted up in the usual way for the evolution of hydrogen. This has its delivery-tube passed into a tube filled with fragments of calcic chloride, for the purpose of absorbing the moisture which may be carried over with the gas; to the other end of this drying tube is connected the tube which is to hold the metallic oxide (generally

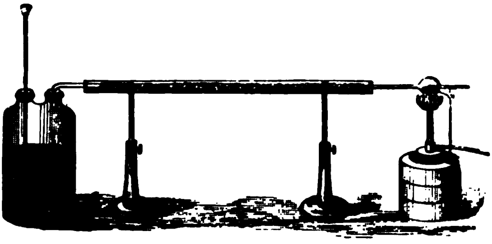

Fig. 7.

in a bulb blown upon this). The gas-bottle should contain about a couple of quarts, so as to afford a steady supply, and the calcic chloride tube should be long and well filled. In operating, after the gas has completely driven out the air in the apparatus, heat is applied to the bulb containing the oxide, and so its reduction will be brought about. The gas must be kept up in a good stream, so as to drive out the watery vapour formed by the decomposition. Here the hydrogen takes the oxygen of the oxide, and water is formed, while the metal is set free. All metals whose affinity for oxygen is lower than that of iron may be thus reduced; indeed, oxide of iron may itself be so treated; but, in this instance, these affinities are just balanced: for, on the other hand, if we heat a quantity of iron filings in a glass tube, and then pass the vapour of water over them, we get the water decomposed, its oxygen oxidizes the iron, and its hydrogen is evolved. It is a fact worthy of notice here, that almost all metals so reducible by hydrogen may also be reduced by the dry distillation of their oxalates. Carbonic acid, and sometimes water, is given off from the decomposition of the oxalic acid, and the metal in a pulverulent state is left.

All metals, too, which are reducible by hydrogen, are equally so by carbon.

In the case of metals whose affinity for oxygen is greater than that of those reducible by the above means we have a powerful method in the use of a second metal whose affinity for oxygen exceeds that of the one we wish to reduce. Thus, if we heat potash very strongly in contact with iron, we reduce the former, and set free potassium in the state of vapour, which may be condensed into the metallic state. But, in these cases, temperature has much control over the course of affinities. For, if we, on the other hand, mix oxide of iron with potassium, and heat gently, we have the iron deoxidized and potash formed.

Some oxides will be reduced by heating with sulphur. Thus the latter is oxidized, and passes off as sulphurous acid. But the oxides become either sulphides or mixtures of sulphides and sulphates. Again, chlorine gas will reduce some, as gold and platinum oxides, in which cases the metals are set free. But in other cases the metal, in place of actual reduction, is converted into its chloride. But the gas must be dry.

Lastly, there are metals whose affinity for oxygen is so strong as only to be overcome by the force of the galvanic current, and there are few bodies which can resist its decomposing influence. The *sine quâ non*, however, being that, in order to decompose them, they must (to a certain extent, at least) be soluble in water. The most simple exhibition of this force is made in taking a metallic solution, as of a salt of copper, for example, and plunging into it a strip of clean iron. The latter, having a greater affinity for the acid than the copper has, begins at once to be acted upon, and to be dissolved, especially if the solution be slightly acid. The iron replaces the copper in the combination, and the copper is thus set free and deposited at the point of action, viz. the surface of the iron dissolving; and this would go on until all the copper was reduced and removed from the solution and replaced by iron. And, moreover, the changes would take place in the relative atomic weights of the two metals; and so for every 63·5 parts of copper reduced, 56 of iron would be taken into solution.

Electrical action has much to do with this. The slight acidity of the solution first determines the solution of the iron, and the moment the least film of copper is deposited on it, the copper becomes the negative, and the iron the positive element of a voltaic arrangement; and subsequently the decomposition of the salt is thus carried on until its completion.

The metals are often deposited in this way in beautiful dendritic crystals, as, for instance, in the case of the lead tree, where a solution of a lead salt is reduced by the introduction of a plate of zinc.

Light suffices to decompose the oxides of the noble metals. Thus, a glass vessel containing a solution of gold will deposit the gold in an increasing film on the side next the light. But Berzelius and some others consider that this action may be due to light in its connexion with electricity.

Metals with Chlorine.—Between the metals and the gas chlorine a most powerful affinity exists; indeed, exceeding that for oxygen. If we throw portions of any which can be finely divided (by powdering or otherwise) into a jar of chlorine, we get all the phenomena of combustion, light and heat being evolved. In the case of most other metals, as may be shown by iron, a very slight rise of temperature suffices to cause this inflammation; and even the noble metals, which resist the action of oxygen under the same circumstances, will slowly and quietly absorb chlorine, if placed in it.

Most of the chlorides have the physical appearance of salts; some have a tough, horny appearance: they vary in colour, and but with a few exceptions, are soluble in water. Some few are quite insoluble. Argentic chloride, and mercurous chloride for instance; while some, like antimonious chloride, are decomposed on adding water to them.

Several methods of obtaining chlorides may be employed.

First. All metals, when heated in chlorine, will combine with it, the heat evolved during chemical union being in general sufficient to fuse off the chloride formed, otherwise the metal would soon be protected by it from further action of the gas; thus the iron or antimony perchlorides may be prepared.

Second. The oxide of a metal may be mixed with charcoal, and then, by passing a current of dry chlorine over this, the oxygen will be taken by the charcoal to form carbonic oxide, while the metal combines with the chlorine.

This plan is employed where the resulting chloride is volatile, as aluminium and titanium chlorides, which volatilize and condense in a cool part of the apparatus.

Third. Some sulphides are decomposed by a current of gaseous chlorine, which chlorinates both the sulphur and the metal: a metallic chloride and chloride of sulphur being the result. Or dry hydrochloric acid may be similarly used with a sulphide or an oxide.

Fourth. Hydrated chlorides may be prepared by dissolving a metal in hydrochloric acid, when it at once displaces the hydrogen, combining with the chlorine; or an oxide or carbonate may be employed. The solution obtained may in most cases be crystallized; but in some evaporation cannot be carried on in contact with the air without decomposing the chloride. Thus aluminium and magnesium chlorides will lose their chlorine if so treated.

But there are cases where hydrochloric acid will not dissolve a metal, and where for forming such chlorides the gas must be brought to act on the metal in a nascent state; thus the chlorides of gold and platinum are only obtained by the employment of *aqua regia*, where the nitric acid sets free chlorine from the hydrochloric, in such a state that it will at once combine with the metal; the latter being dissolved, all excess of nitric acid is got rid of by evaporating the solution to dryness, adding a little hydrochloric acid from time to time during this evaporation. The pure chloride being subsequently got by solution of the residue in water.

Lastly, metallic chlorides, which are insoluble in water, may be precipitated by adding to any soluble salt of the metal an alkaline chloride, or hydrochloric acid. Thus argentic chloride is obtained; and, in like manner, plumbic chloride and mercurous chlorides are formed.

Strongly basic metals, such as sodium, will readily reduce chlorides of more electro-negative ones. Thus sodium, when heated with aluminium or magnesium chloride, will become sodic chloride, and set free the magnesium or aluminium. And thus such metals, whose oxides we are unable to reduce, are readily procured from their chlorides. Similarly we may act upon tin, antimony, or bismuth, with mercuric chloride, and obtain the transference of its chlorine.

In reducing the chlorides, if we except those of gold and platinum, heat has no effect,—not even if charcoal be added, provided the mixture be dry; but if moisture be present, decomposition is at once set up, hydrochloric and carbonic acids being formed, and the metal set free. Sulphuric acid decomposes them, but here the metal is not set free, but oxidized at the expense of the oxygen of the water.

If we except the metals of the alkalis and earths, all other metallic chlorides may be decomposed by heating them in a current of hydrogen ; but the evolution of the latter must be well maintained, so as to drive the hydrochloric acid formed out of the reduction-tube, or it would react upon the freshly-separated metal, and the old state would be restored. Ferrous chloride, when thus treated, affords fine cubic crystals of iron.

Lastly, some chlorides may be decomposed by heating them with a metal which has more powerful basic properties. Thus aluminium is obtained from its chloride by heating the latter with sodium.

The elements iodine and bromine being analogous to chlorine in their actions and habitudes, their union with the metals may be effected in similar ways. The insoluble ones (probably the more important) may thus be obtained by the addition of the iodide or bromide of potassium to the metallic solution, when the iodide or bromide (as the case may be) will be precipitated, just in the same manner as the corresponding chloride.

Metals with Sulphur.—The sulphides are very analogous to oxides, and in considering combinations of the metals with sulphur, it must be first mentioned that such union is very common in nature; and hence many of the ores of the most important metals are sulphides; and it is from such compounds that we derive our chief supply of copper, lead, mercury, silver, antimony, and several others.

In the native state, the sulphides are brittle solids, quite opaque, and in many cases possessing a strong metallic lustre. This latter quality is so marked in some, that, in the case of iron pyrites (ferric sulphide), from colour and lustre it has frequently, by inexperienced persons, been mistaken for native gold. They are often found crystalline, and of those not naturally so, many may be crystallized by fusing them. And they are almost all fusible.

With the exception of sulphides of the metals of alkalies, and alkaline earths, they are all insoluble in water. As already mentioned, some may be fused, and of these many will sublime unchanged; but, in the case of some containing more than one proportional of sulphur, such treatment will reduce them to the state of protosulphides, as happens with tin and iron disulphides.

The method of forming vermilion is a good example of the ease with which some sulphides sublime. The metals, in many instances, form several sulphides: thus potassium, for example, combines in five proportions with sulphur. As with the oxides of metals we get a class where, by union of a metal with oxygen, an acid is formed capable of neutralizing and forming a salt with a basic oxide, so with the sulphides we have precisely an analogous state of things; and certain metallic sulphides will act as acids towards others which have basic properties. This is the reason of the non-precipitation of some metals by ammonio-hydric sulphide, viz. the sulphide of the metal formed by it combines with some undecomposed ammonio-hydric sulphide, and forms a soluble salt. Thus, if we add the latter reagent to a solution containing gold, the metal is precipitated as a sulphide, but it will be immediately thus redissolved by an excess of the alkaline sulphide.

They may be artificially formed in the following ways:—

First. By heating a metal or an oxide with sulphur. Thus, if iron filings and sulphur be projected into a hot crucible, the latter being kept at a dull red heat, an appearance of combustion ensues,—an evidence of the violent action taking place,—and there will remain a metallic-looking residue, a protosulphide of iron. But where an oxide is heated with sulphur, the former is decomposed, and its oxygen with some of the sulphur forms sulphurous acid, which is evolved. Again, with alkaline earths, or alkalies, so treated, the resulting sulphide will contain portions of sulphate, and also of uncombined sulphur. Indeed, in both instances, viz. of metals and of oxides so treated, we obtain compounds by no means definite, and commonly containing variable proportions of uncombined sulphur.

Some sulphides, and in some cases sulphur salts, are formed by heating a mixture of metallic oxide and sulphur with potassic carbonate. If this be done in a crucible lined with charcoal, the metallic oxide is reduced, the sulphur combining first with the alkali forming an alkaline sulphide, which is subsequently decomposed at a red heat, and affords its sulphur to the metal, to convert the latter into a sulphide.

Some sulphides may be obtained by heating a sulphate to redness with charcoal, or by heating it in a glass tube, and then passing a current of dry hydrogen gas over it. In the first process, the charcoal takes the whole of the oxygen, and so carbonic oxide is formed and evolved, the sulphide being left.

$$\text{Thus, Met. } SO_4 + 4\,C = \text{Met. S.} + 4\,CO.$$

Where the operation is effected by hydrogen, the whole of the oxygen is separated, as in the last case, and water is the secondary product. But in many cases some of the sulphur is lost, and metallic subsulphides result. Indeed it is only the alkali metals which thus give true protosulphides.

Hydrosulphuric acid (dihydric sulphide) is a ready agent in the formation of metallic sulphides. Thus, if we pass it over a heated metal or oxide in a glass tube we obtain the sulphide, and carbon bisulphide may also be employed in the state of vapour in a similar way. With carbon bisulphide and a metallic oxide, the reaction produces a metallic bisulphide and carbonic acid.

If hydrosulphuric acid (dihydric sulphide) or an alkaline sulphide (in some cases), be added to solutions of metallic salts, a sulphide of the metal will be precipitated. As by one or other of these all the metals, excepting those of the alkalies, alkaline earths, and earths proper, may be so precipitated, and moreover, as the resulting sulphides are very characteristic in each, these reagents afford the means of analysing metallic solutions. By them, and potassic carbonate, the whole category of metallic bases may be classified, and, moreover, by means of these three reagents alone. Thus, to a solution of a metallic salt, or salts rendered slightly acid by the addition of a little hydrochloric acid, hydrosulphuric acid (dihydric sulphide) is first added; this will precipitate, as sulphides, any metals present belonging to a large first group of something like twenty metals. Next, having separated the precipitate, and rendered the acid solution slightly alkaline, by adding some ammonia, the addition of an alkaline sulphide, as sulphide of ammonium (ammonio-hydric sulphide) will precipitate any metals of a second group, also as sulphides. These removed, the addition of potassic carbonate precipitates a third group; while, lastly, a small group, consisting only of four, or in some cases five, will remain untouched by either of the three precipitants mentioned.

The colour of the sulphides of some of the metals, thus precipitated, is very marked. Those of the noble metals, as also of lead, bismuth, copper, iron, cobalt, and nickel, are all black. Molybdenum, vanadium, tungsten, and tin (when in the state of protoxide) afford brown sulphides; antimony, a reddish orange one; cadmium, orange; arsenic, orange-yellow; tin (when it exists as peroxide), yellow; manganese, flesh-coloured; and zinc, a white sulphide.

In reducing sulphides, some few are reduced by heat alone, as gold and platinum. Silver sulphide is also thus reduced, but at the same time partially oxidised, so that a small portion of argentic sulphate is formed. This, however, is to be reduced also by considerably raising the heat used.

In the reduction of many sulphides by so heating in the air, the sulphur evolved by union with oxygen becomes sulphurous acid; but another portion of oxygen combines with the metal, and we get an oxide left, in the place of the metal itself.

The smelting of many ores may be resolved into just these changes, of which copper ores may be given as a good example. Sometimes the application of heat and air converts the sulphide, first into a sulphate, when, if the new compound be capable of sustaining the temperature, it remains permanent; but, if not, it passes to the state last described, viz. separation into sulphurous acid and a metallic oxide.

Many reducing agents may be employed to combine with the sulphur, as metallic iron, hydrogen, chlorine, &c. Thus, if we heat sulphides of lead or copper with iron, sulphide of iron and the metal results. Galenas are often assayed this way, clean iron nails with a little black flux being used. This method will be described in the article upon lead.

Some few sulphides will be reduced by passing dry hydrogen over them at a red heat, the metal being reduced, while the sulphur combines with the hydrogen, and forms hydrosulphuric acid (dihydric sulphide). Thus sulphides of antimony, bismuth, copper, tin, and silver are decomposed.

Dry chlorine gas will likewise decompose them, and both the metal and the sulphur will combine with it; and they may also be converted into chlorides by nitro-hydrochloric acid; some few also by hydrochloric acid. In the latter case, the hydrogen of the decomposed acid combines with the sulphur of the sulphide, and is evolved as dihydric sulphide. One of the means of obtaining the latter body for use as a reagent consists in heating antimonious sulphide in hydrochloric acid, or by treating ferrous sulphide with dilute sulphuric acid, and without heating.

In the first case, the decomposition will be shown by the following formula: $Sb_2\,S_3 + 6\,H\,Cl = 2\,Sb\,Cl_3 + 3\,H_2\,S$. In the second, where ferrous sulphide is used, the iron simply replaces the hydrogen of the acid, which, taking the sulphur set free, forms the gas. The formula is $Fe\,S + H_2\,S\,O_4 = Fe\,S\,O_4 + H_2\,S$.

Lastly, they may be decomposed by means of strong nitric acid, a method employed in many cases of analyses of ores; as, for instance, copper pyrites, galena, blende, and some others. The powdered mineral is treated with strong nitric acid, whereby its sulphur is more or less completely oxidized (the extent of oxidation depending much upon the time employed in digestion). All that portion which is not thus converted into sulphuric acid separates in yellow masses, which by continuance of heat fuse into yellow beads. The liberated metal combines with undecomposed acid to form a nitrate. Native cinnabar, or mercuric sulphide, is the only ore which cannot be so treated.

The simple body, selenium, precisely resembles sulphur in its chemical relations: hence it combines with metals much in the same manner. Native selenides are found, but very rarely.

Phosphorus combines with metals, forming the class phosphides,—an unimportant one. They may be formed by fusing a metal, and then throwing phosphorus into the crucible in successive portions, when direct union takes place. Or if a metal, or its oxide, be heated with phosphoric acid and charcoal, the carbon will take the oxygen of the acid, while the phosphorus, set free, combines with the metal. Where the oxide has been employed, its oxygen appropriates another portion of carbon, also for the formation of carbonic acid.

Some phosphides may be obtained in the wet way, like the sulphides, viz. by transmitting phosphuretted hydrogen gas through a solution of the metallic salt. Thus, if we dissolve cupric sulphate and so treat it, we get a black flocculent precipitate of cupric phosphide; but it is soon decomposed by exposure to the air. It is said that a corresponding silver salt may be formed, but this is doubtful.

If a phosphide be heated in the air, it will absorb oxygen, and be converted into a phosphate; at other times the metal is set free, and the phosphorus, in this last case, alone oxidized.

As the quantitative analysis of the three principal classes of compounds just considered,—viz. oxides, chlorides, and sulphides, is often required, the methods may now be briefly considered here.

In metallic oxides, the amount of metal and of oxygen may both be estimated by one operation. An accurately weighed portion is heated in a bulb tube, and a current of perfectly dry hydrogen passed over it, just as described at page 41; but a small tube containing calcic chloride, as used in organic analyses, is also carefully weighed before the operation, and then attached to the reduction-tube, so as to receive and retain the water formed by union of the hydrogen with the oxygen of the oxide. The operation over, the metal is weighed, and the loss reckoned as oxygen; but this is also checked by weighing the calcic chloride tube, and from the weight of water found, calculating the amount of oxygen liberated.

Where the method is inapplicable, a known weight of the metal may be converted into nitrate by nitric acid, and then heated carefully, so as to drive off the acid of the salt, when the oxide remaining may be weighed.

Chlorides are always estimated by separating their chlorine as argentic chloride. If soluble, the chloride is dissolved in water; a few drops of nitric acid are added, and then an excess of argentic nitrate. The precipitated argentic chloride is then collected and weighed. If the chloride is insoluble, as in the case of plumbic or mercurous chlorides, it is first to be boiled with caustic potassa: the result of this decomposition will be the formation of soluble potassic chloride; and from this the chlorine may now be estimated, as before, by means of argentic nitrate, by precipitating from the filtered solution.

In analysing sulphides for the estimation of sulphur, they may be decomposed by means of aqua regia. By this much of the sulphur is oxidized, and converted into sulphuric acid; while some is sure to separate unchanged, appearing as oily yellow beads in the solution. The liquid is therefore filtered, and the latter estimated by carefully drying the filter and weighing; after which it is heated sufficiently strongly to drive off the sulphur, and then again weighed; the loss of weight gives the quantity of sulphur unchanged. The filtered solution is then precipitated by baric chloride or nitrate, and from the weighed precipitate of baric sulphate, the remaining sulphur is calculated, and added to the amount before estimated. Thus the total amount contained in the sulphide under examination is arrived at; 100 parts of baric sulphate will correspond to just 13·74 of sulphur.

CHAPTER III.

METALLIC SALTS AND ALLOYS.

THE views concerning the formation, constitution, and character of the class of bodies known as metallic salts, have undergone many changes as chemical knowledge has advanced, but it may be well briefly to review the older opinions upon their nature, before stating those held at present.

Any body composed of an acid and a base and capable of being crystallized was called a salt, and salts were commonly obtained by saturating an acid with a metallic oxide; or by dissolving a metal in acid, and an early division was into neutral, acid, and alkaline salts.

But the division in this manner by Berthollet was most fallacious; and in illustration of this, it may be stated that a salt may appear to be neutral solely from its insolubility. Again, a neutral salt, when soluble, will, in many cases, appear alkaline, as in the case of alkaline carbonates; while, thirdly, true heavy metallic salts, if they contain enough acid to make them soluble, will appear acid, although really neutral. The test employed to ascertain these conditions is usually the action of solutions of the salts upon vegetable colours. Thus the blue tint of litmus will be immediately reddened by a trace of acid, and the red again restored to blue by an alkali. Or, in the latter case, if a paper stained yellow by turmeric be used, it will be browned, and capable of being again restored by acid.

The red colour produced in the litmus is from the setting free of its own acid, for it may be said to be a salt of a peculiar acid united to a feeble base, and this latter being taken by the stronger acid of the salt under examination, the litmus acid is liberated.

Subsequently the terms neutral, acid, and alkaline, were applied to salts under other conditions, and a salt was regarded as neutral, only when the number of atoms of acid entering into its composition exactly equalled the number of atoms of oxygen contained in the base, as shown, for example, by the two iron sulphates, which according to the old formulæ and symbols would be represented as $Fe\,O, S\,O_3$ for ferrous sulphate, and $Fe_2\,O_3, 3\,S\,O_3$ for ferric sulphate. Then where an acid combined in two proportionals with one of base an acid or super salt was formed, while, on the other hand, one proportional of acid with two of base was said to produce a sub or alkaline salt.

The first class or neutral were also termed normal salts, when formed on the type above described.

In classifying salts they were also divided into oxysalts, and hydrosalts or haloid salts. In the first an oxyacid as sulphuric, for instance, was said to combine not with a metal, but with its oxide as symbolized above in ferrous sulphate or $Ag\,O, N\,O_5$ argentic nitrate, $Cu\,O\,SO_3$ cupric sulphate and so forth.

But inasmuch as it was found that the second class were not composed of a hydro-acid as hydro-chloric, united with a metallic oxide, but were really compounds of the radicle of the acid with the metal itself, these were further termed haloid salts, as resembling sea salt in constitution. For if soda be saturated with hydro-chloric acid, and the resulting salt crystallized, it will on examination be found to be a compound of the chlorine or radicle of the acid, with the sodium or metal of the alkali. The hydrogen of the acid with the oxygen of the base having combined to form water, thus according to present formulæ $Na_2\,O + 2\,H\,Cl = 2\,Na\,Cl + H_2\,O$.

But in simplification of these views came the binary theory of salts, first put forward by Sir H. Davy, and subsequently worked out by Daniell, Graham, and others. They considered that as an anhydrous acid, such as sulphuric or nitric acid, $S\,O_3$ or $N\,O_5$ has no acid properties until combined with water, as $S\,O_3 + H\,O$, or

$NO_5 + HO$ (using the old formulæ for these acids), they might therefore be regarded as acid radicles combined with hydrogen, and represented thus as HSO_4, and HNO_6. Assuming this, the formation of salts, both in the case of hydro and oxyacids, is brought about by the simple displacement of the hydrogen in each case, by an equivalent quantity of a metal.

We now indeed write these acids as H_2SO_4, and HNO_3, and views very similar to the above are those now held by chemists as to the constitution of these bodies; thus Odling says, 'Bodies obtained from acids by displacement of a metal for hydrogen are characterized as salts;' and Miller, 'Most chemists now regard what were hydrated acids as a salt which is a compound radicle, the oxion of the salt (consisting of an anhydride + 1 of O), united with an equivalent of H, other salts of the acid being formed from these hydrogen compounds by displacement of the H by an equivalent of metal.' The following formulæ may be now given to show the identity of the reaction in the cases of hydrogen acids; thus, if we add hydro-chloric acid to zinc, $2\,HCl + Zn = ZnCl_2 + H_2$ evolved, and if sulphuric acid then:—

$$H_2SO_4 + Zn = ZnSO_4 + H_2$$

If, however, in place of employing a metal we act upon its oxide by the acid, in such case, instead of evolution of hydrogen, we have the hydrogen combining with the oxygen of the oxide
al with consequent production of a proportion ^ of water.

$$\text{Thus } 2\,HCl + ZnO = ZnCl_2 + H_2O,$$
$$\text{And } H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

Lastly, there is also a small class of salts first described as such by Berzelius, and termed by him sulphur salts. For sulphides of positive metals will in some cases combine with sulphides of negative ones. Thus potassic sulphide unites with arsenic sulphide, or again, ammonic sulphide with auric sulphide. The potassic sulphide and the ammonic sulphide acting as bases, while the arsenic sulphide and auric sulphide play the part of acids.

Sometimes we get such sulphur compounds capable of crystallization, soluble in water, &c., and with other characteristics of salts; but often they are decomposed by water. Indeed, they do not constitute at all an important class.

Salts combine with each other, and produce a class called double salts. In these, two distinct bases are united with one acid. It may be, first in the way of the combination of two neutral salts of the same acid, as, for instance, cupric sulphate with potassic sulphate. In such a perfectly definite crystalline salt may be obtained by dissolving and mixing together atomic proportions of the two component salts.

Again, ferrous sulphate and cupric sulphate may be united; and although the crystals of the first contain 7 proportionals of water, while those of the latter contain 5, so complete will be the union that the new salt will agree in this respect with the one containing the larger amount of water.

When a metallic salt has been formed by the solution of a metal, the simple evaporation, so as to drive off a portion of water, causes it to assume the solid state in certain regular mathematical forms, called crystals; and these forms are always the same (with certain modifications) in the same salt. Thus ferrous sulphate always crystallizes in oblique rhombic prisms; cupric sulphate in rhombohedral forms; argentic nitrate in four or six-sided tables; sodic chloride in cubes; baric chloride in flat, four-sided crystals, bevelled at their edges;—all, it will be perceived, distinct and, in the same salt, constant forms.

In cases of artificial crystallization, the more slow the process, the finer and more definite will be the crystalline forms. Hence, by exposing a strong solution to the air, so as to allow the water to evaporate spontaneously, we fulfil the conditions to perfection; and we therefore find in nature crystalline forms the most perfect where the deposit of solid matter has been so exceedingly slow that it is effected in the most regular manner: thus many of our ordinary ores contain most beautiful crystalline portions, some being entirely crystalline; and even the metals themselves are frequently found native in perfect crystals.

It has been stated that the same salts crystallize uniformly in the same definite forms; but this law admits of exceptions, the reason of which may be here explained.

If we take an ordinary crystal, and with a knife attempt to split it, it will be found that this can be effected only in certain directions, and in such a clean facet will be obtained; but in all others (if we succeed at all, and do not actually crush it) we get only an irregular, broken surface. Now the planes in which the operation can be effected are called planes of cleavage; and as all crystals have one or more imaginary axes, around which their particles are supposed to have been built up, we can cleave a crystal around these in the same relative directions, until we have altered its mathematical form altogether, and obtained an equally regular second one, which would hence be called the secondary form of the crystal.

Suppose, for example, a cube be taken, and starting from a central point upon its upper face, the four solid angles be cleft off successively, the cleft surface being formed in each case from the point just mentioned, down to the centre of each edge; then, if we turn the crystal upside down, and repeat the operation, starting from the same point of the opposite face, a regular octohedron would result. Again, by similar means, but by removing the twelve edges of the perfect cube, instead of the angles, we should obtain the dodecahedron; or, lastly, from the same primary form, a tetrahedron may be obtained, by cleaving off alternate angles only.

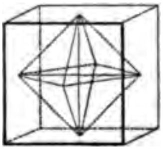

Fig. 8.

Now it will be readily perceived, that in nature's laboratory a slight disturbing force may frequently come into play during the aggregation of particles going to form a crystal, and may hence interfere with the completion of the perfect primary form. Thus a great variety of secondary ones will arise, for in the progress of building up a crystal, which is, of course, the reverse action to the kind of dissection above described, we may see how growth may accidentally be stopped in some directions; indeed, it very commonly is so; and hence we seldom get either primary or secondary forms quite perfect. But the disturbing force being some internal one, acting upon the ultimate particles, has influence alike upon all parts around each axis, except where hindered by external interference, as where a crystal rests upon the vessel in which it is forming; otherwise the modifications produced are symmetrical on all sides, from which fact the crystalline axes are called 'axes of symmetry.'

The secondary forms which calcic carbonate assumes in nature may be instanced to illustrate the great extent to which these may be carried, for about fifty distinct forms have been examined and measured. But, in all cases of secondary forms, there are always two or three which are more common than others, and which are hence called governing forms.

Crystals have been classed into six systems, the classification being founded upon the position of their parts in reference to their imaginary axes.

Calcic carbonate has been mentioned as an instance of great variety of secondary forms, but amongst these some belong to different systems, which forms are consequently incompatible; that is to say, you could never, by cleavage of the one, obtain the secondary form of the other. Such salts are said to be dimorphous in form.

On the other hand, where substances assume the same crystalline form, although differing in chemical composition, they are said to be isomorphous. Thus it will be evident that the composition of a compound cannot be decided upon by the simple knowledge of its exact crystalline form, as was formerly supposed.

During the formation of crystals a large amount of water is taken up with them. One portion is necessary in giving and preserving crystalline form, and this is called water of crystallization. A second portion is necessary to the actual existence of the salt, and hence is called constitutional water. The difference between these may be explained in the case of crystals of zincic sulphate. These contain 7 ~~equivalents~~ of water. Now, if they atom
are heated to 212° F. = 100 C. 6 ~~equivalents~~ are driven off,

and the form of the crystal is destroyed, but the remaining one is retained firmly united; if, however, the heat be carried up to about 410° F. = 210 C., we separate this remaining one also. The first six are water of crystallization, the seventh, water of constitution.

In the case of some salts the water of crystallization is held so loosely that the simple exposure to air (especially dry air) suffices to set it free; and the result is, that crystalline structure is lost, and the salt crumbles down to a complete powder. This is called efflorescence.

Salts differ very widely in their affinity for water, or, in other words, in solubility. Some have so great an affinity for it, that they will even melt in the water of crystallization: these are said to deliquesce. On the other hand, others require so large a quantity of water for solution, that they are nearly insoluble; while many are quite so.

But the solubility of a salt varies very much with the temperature of the water employed; and this property, added to the fact that salts also differ very widely in their solubility amongst themselves, affords us a ready means of purifying many metallic salts. It is, for this end, only necessary to take the crystals of a salt, dissolve them in boiling water, and filter the solution, so as to separate any mechanical impurities; then to set the solution aside: as it cools crystals will be reformed. These are to be taken from the solution, or mother liquor, drained, and again dissolved and crystallized; and after two or three such operations the salt will generally be found tolerably pure, the impurities being retained in these mother liquors.

If, however, the process be slow, the crystals will be large, and apt to retain a quantity of mother liquor in their interstices, and hence will be less pure than quicker formed compact crystals.

Water is frequently mechanically enclosed in the structure of a crystal, and, where this is the case, it will fly to pieces with a crackling noise, upon being heated. Such salts are said to decrepitate; and it is found that decrepitation is loudest in those which contain no water of crystallization.

If it be desired to obtain large crystals of a salt, it may be effected in proportion as we cool down the solution very gradually, or allow the evaporation of a less saturated one to go on slowly. Thus manufacturers sometimes cover crystallising vessels with non-conducting substances, so as to allow of time for slow crystallization; for where this takes place rapidly it is always more or less confused.

In slowly growing crystals, as this operation may be termed, light has a singular influence, for it is found that the crystalline axes always turn towards it.

Crystals form better when the containing vessel of the solution has a rough surface, so as to afford points whence the action starts; and it is sometimes found that, even when the solution contains more of the solid salt than it is ordinarily capable of dissolving, yet crystallization will not be set up; but, in such a case, the introduction of a stick or piece of string will at once determine the action, by withdrawing a small portion more of the water, when the salt, receiving this impetus, will at once crystallize round this foreign nucleus.

Many metallic compounds may be sublimed, that is, volatilized by heating; and as their vapour cools it redeposits, and commonly in crystalline form: thus ferric chloride, mercurous and mercuric chlorides, and arsenious anhydride (arsenious acid) may be crystallized by sublimation.

The metals themselves may, in very many cases, be obtained in crystals, and by analogous plans to those pursued in salts, viz. rendering them fluid, and causing their solidification to take place very slowly: thus bismuth is often got in most beautiful regular forms. A quantity is melted in a ladle, and the ladle then placed in some hot coals, a dish also covering it, and containing similar hot fuel. In this way cooling goes on very slowly, and when a crust has formed on the surface it is pierced, and the portion in the centre yet remaining fluid is quickly poured out. The mass is then found, on opening it, lined with crystalline forms.

Tin may be also crystallized by slow cooling after fusion.

The author has also crystallized gold by allowing a melted mass to solidify very slowly—in fact, for some hours letting down the temperature to the point. Then, by dissolving out the surface metal by a menstruum having but feeble power of action, the crystalline structure of the interior is developed.

Gold and silver are also frequently obtained in crystalline form by slow reduction from their compounds. They are also frequently found in the native condition crystalline.

Lead may be crystallized by fusion and slow cooling, as in Pattinson's operation, the crystals being comparatively pure; but antimony, which is commercially found crystalline, is so, dependent upon its impure condition; for Matthiesen has shown that pure antimony does not crystallize.

Lastly, crystalline form in a metal often results from slow action during its electro-deposit: thus, as will be hereafter shown, tin may be obtained in beautiful dendritic crystals.

The metals crystallize either under the cubic or the rhombohedral systems.

Alloys.—Compounds of metals with each other will retain all the physical properties of pure metals, but always in very modified degrees. Such compounds are called alloys, but where mercury enters into the combination, and consequently the mixture is more or less fluid or pasty in texture, they are then termed amalgams. Few metals as commonly met with are free from mixture of others, although the foreign one is commonly in very small proportion; but as pure metals are rarely fit for mechanical or economic uses without alloy, such additions are usually made as by experience are known to render them fit for their required uses.

Although we do at times find alloys in nature which are formed in definite proportions, and are true chemical compounds, yet they are, as commonly formed, simple mixtures of the constituents, and hence may be made in any relative proportions. This state of union often gives them a great tendency to separate; and thus in some alloys of silver and copper we find certain parts of a bar formed of them uniformly richer in silver than the other parts. In such a case the separation is but slight and partial, a small portion only of the alloy flying off towards the edges of the bar, and rendering that part poorer. But sometimes the mixture of two metals is so purely mechanical that if a fused portion be allowed to stand, the components will separate, and the one possessing the highest specific gravity will subside to the bottom, while the lighter one rises to the surface in the melting pot. This separation, however, is rarely quite complete, for each metal will retain a portion of the other. Thus Matthiesen found that on melting equal parts of lead and zinc, and after well mixing, allowing the alloy to cool slowly, they separate, but the heavier lead on subsiding retains 1·6 per cent of the zinc alloyed with it; while on the other hand, the upper layer of zinc thrown out retains 1·2 per cent of lead. And bismuth and zinc similarly treated separate in like manner, the upper zinc alloying with 2·4 per cent bismuth, while the lower layer of bismuth retains 9 to 14 per cent of zinc.[*]

In his two elaborate papers, he says, 'A solid alloy may be, 1st, a solidified solution of one metal in another; or 2nd, a chemical combination; or 3rd, a mechanical mixture; or 4th, a solidified solution or mechanical mixture of two or all of the above.' And he similarly divides the liquid alloys; defining a solidified solution as a perfectly homogenous diffusion of one body in another, illustrating it by glass, which is formed in the liquid state at a high temperature, and solidifies on cooling without separation of the different silicates.

It has been said that physical properties are modified in alloying metals. Thus colour is more or less affected. It may often be such as would result from the combination of the colours of the metals forming the alloy; as, for example, the yellow of brass, where zinc a bluish metal is mixed with the orange red copper. But it is also often very widely different. Thus gold with any quantity of silver,—three parts of silver to seven of gold, for instance,—gives a pure green alloy. Again a small quantity of nickel, a grey metal, when added to brass, will produce an alloy of almost silvery whiteness; and many similar examples might be given.

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[*] Report on the Chemical Nature of Alloys. From the *Report of the British Association for the Advancement of Science for* 1863; also 'On Alloys,' *Journal of the Chemical Society*, 1867, page 201.

Hardness is much affected, and usually increased. Thus the mixture of the two soft metals tin and copper will produce a very hard alloy. One part of tin to two of copper is exceedingly hard, and consequently susceptible of so high a polish as to be employed for the reflectors of telescopes, &c., under the name of speculum metal.

Copper with zinc in proper proportion, will give a brass affording a wire, which when hard drawn is almost equal to steel for small springs, and in some cases of more useful application. And a small per-centage of tin increases its hardness. But a small per-centage of lead will quite destroy its ductile property, although it renders the brass more fit for turning purposes.

The addition of alloying metals to silver or gold, for the formation of plate or coin, is merely for the purpose of giving them hardness equal to resisting the effects of wear upon them. But the hardening may be carried too far, and an alloy then results which abrades and grinds away under wear. What is required in such cases is a judicious mixture of metals, which, while affording sufficient hardness, retains to a great extent the tough condition of the principal metal. Thus a much more durable coin is produced, as, for example, in our old guinea, where the gold was standarded by copper and silver in equal proportions, from the fact of such an alloy producing the required condition to perfection.

Malleability, ductility, and tenacity are often much modified in metals by their being alloyed, the two former being diminished by it; indeed, an alloy of two ductile and malleable metals will frequently become very brittle. Thus a mere trace of lead (itself malleable), when added to gold, will entirely destroy the malleability of the latter, rendering it quite brittle.

A brittle and a ductile metal generally afford a brittle alloy; and so antimony, when added to gold to the extent only of 1900th part, will make the gold quite unworkable from its presence, although in such small proportion.

Tenacity is usually very much increased, and in Matthiesen's experiments upon this the following curious results were obtained, employing wires of the same guage the following weights ruptured the wire : —

Copper	25–30 lbs.	Copper with 12 per cent. Tin	80–90 lbs.
Tin	under 7 „	Tin with 12 per cent. Copper, about	7 „
Lead	under 7 „	Tin with Lead . . . under	7 „
Gold	20–25 „	Gold with Copper . .	70 „
Silver	45–50 „	Silver with Platinum . .	75–80 „
Platinum	45–50 „		
Iron	80–90 „	Steel (or Iron with Carbon) above	200 „

It might be expected that a mixture of two metals would have a specific gravity, the mean of the two; and this is sometimes true, but by no means universally so, for in some cases condensation takes place, and so we get the specific gravity increased ; at others expansion, which correspondingly diminishes the specific gravity. But the remarks made at p. 24 upon the method of calculating the specific gravity of alloys must be borne in mind also in estimating them.

Alloys are generally more readily oxidizable than their constituents ; and the superior oxidizability of one constituent of an alloy appears to be assisted by galvanic action set up. This is always the case where an electro-negative, or acid-forming metal, is alloyed with an electro-positive, or base-producing one. Chemical action is therefore generally more energetic on an alloy than upon a simple metal ; and indeed metals which are untouched by an acid when alone, will be acted upon by the same acid, when alloyed with another which is soluble in the acid employed. Thus platinum is quite insoluble in nitric acid, but if it be alloyed with a large proportion of silver, it will be dissolved with the silver by the nitric acid, and that to the extent of a tenth of the weight of silver.

Atmospheric oxidation is likewise more active upon a fused alloy, and hence certain precautions are needed in fusing them in order to maintain their composition. In alloys of tin with copper, or with lead, or of zinc with copper, it is better to fuse the metal first which requires the highest temperature for its fusion, and then to add the more easily fusible one; and as a further precaution, to cover the melted surface with a layer of charcoal. And the latter is especially needed in mixtures of gold and copper, or of silver and copper, to prevent oxidation of the copper, and consequent elevation of the standard of the metal, with corresponding loss of weight. And it is perhaps almost needless to remark that all alloys should be carefully stirred, so as thoroughly to mix them just before pouring.

Alloys crystallize equally with pure metals, and in some cases alloying a metal favours crystallization. Thus commercial antimony, which contains small amounts of other metals, is always crystalline; while the pure metal, which is difficult of crystallization, will readily do so on the addition of a very small proportion of tin or zinc. Gold and mercury, and also silver and mercury, both crystallize in four-sided prisms; and indeed it is in those alloys where mercury is present that true chemical combinations are more commonly found. Some have thus been formed by artificial means, as those of mercury with copper, tin, zinc, and lead; and by first forming semi-solid amalgams, and then subjecting them to enormous pressure by the hydraulic press, Joule by such a plan formed amalgams of the following compositions, $HgCu$; $HgFe$; $HgZn$; $HgPb_2$; and $HgSn_7$.

But the existence of these crystalline alloys in definite proportion, is no proof that all such combinations capable of crystallization are therefore necessarily chemical combinations, for many may be found even amongst solid alloys, as in those of gold with tin, where the relative proportions of the metals may be much varied, and yet with the same crystalline form of alloy.

The fusing point of alloys is uniformly lower than the mean of those of their constituents; and Matthiesen says in explanation of this, that 'It is generally admitted that matter in the solid state exhibits excess of attraction over repulsion, whilst in the liquid state these forces are balanced, and in the gaseous state repulsion predominates over attraction. Let us assume that similar particles of matter attract each other more powerfully than dissimilar ones attract each other. It will then follow that the attraction subsisting between the particles of a mixture will be sooner overcome by repulsion than will the attraction in the case of a homogeneous body; hence mixtures should fuse more readily than their constituents.' A most useful practical application of the fact is made in the use of solder for soldering or uniting metals by metal; we usually employ a solder whose base, or main constituent, is the metal we are using it for; and, by the addition of small quantities of other metals, we are enabled to lower the fusing point of the solder in a most gradual and regular way, according to the amount and nature of such addition, by which we adapt it to its particular use, in such manner as that the work itself may remain untouched by the lower heat which is all-sufficient to run the solder.

Some curious examples of the effects of alloying upon the fusing points are afforded in alloys of tin and lead to which bismuth, or bismuth and cadmium are added. Tin melts at 442° F. or 227°·8 C., and lead at 617° F. or 325° C.; now an alloy of lead 3, with tin 1 part, fuses at 541° F. or 283° C., and by increasing the relative quantity of tin it may be diminished yet further in all cases to points much below the mean. But if we add bismuth to the alloy (a metal whose fusing point is 507° F. or 264° C.), we lower it as of such an alloy to about 206° F. or 96°·6 C., that is, below the boiling point of water; and further, by adding a small quantity of cadmium also, we may bring the degree of fusion down to 140° F. or 60° C.

There are some other remarkable points we may notice in this place concerning these lead and tin alloys. Thus, if fused and poured out, just before cooling, the actual partial separation is visible to the eye; for the surface of the metal, if tolerably rich in tin, will be covered with bright spots which if examined are found of uniformly different composition to the surrounding alloy in which they are, as it were enfolded.

Pillichody, of Berne,* has shown too that alloys of tin and lead solidify uniformly at 357° F. or 181° C., and when the solidifying point is looked for, the thermometer immersed in the melted alloy usually exhibits during the passing of the mass from the liquid to the solid state, two stationary points. 'This effect is due to the separation of one or other of the component metals, while an alloy of constant composition still remains liquid. This alloy has the composition Sn_3 Pb. An alloy richer in lead would first deposit lead, and an alloy containing a larger proportion of tin would first deposit tin; the alloy Sn_3 Pb, remaining liquid for a longer or shorter time, and ultimately solidifying at about 181° C. (= 337° F.). This temperature therefore corresponds to the lowest melting point that can be exhibited by an alloy of tin and lead, a larger proportion of either metal causes the temperature to rise.'

The difference of temperature, between fusing and solidifying points, may, as has been suggested, depend on the existence of true chemical combinations of the metals which may be called into existence at higher temperatures, and consequently while they are in the liquid condition, but which suffer decomposition again on cooling down, and that then partial separation takes place again.

Peculiarities in certain alloys will be considered under their respective heads.

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* On Physical Properties of Alloys of Tin and Lead, by Professor Bollers. —*Journal of the Chemical Society*, vol. xv. page 30. Bolley.

CHAPTER IV.

ON HEATING APPARATUS, FURNACES, ETC.

THE various forms of furnaces, and other arrangements for the application of heat, are of the first importance to the metallurgist, not only that they may be effective for the operations required of them, but also that these may be carried out with due economy in the amount of fuel expended.

Although varying in size as seen when the large blast arrangements of iron and other smelting works are compared with the like but small apparatus of the experimental laboratory; or again, when the more recent adaptation of gaseous fuels, both to large and small operations, is looked into, we may observe that the same principles hold good, whether in such large operations or in the miniature ones of the laboratory.

Heating apparatus may be considered under two classes; first, the various methods of applying gases, either specially generated, or else obtained as waste products from the combustion of solid fuels in other operations; and, secondly, furnaces adapted to solid fuels, as in the various forms of melting, reverberatory, muffle, and other furnaces.

Both these classes may be subdivided into wind and blast arrangements. By the former is meant such adaptation of the various parts of the furnace as shall ensure sufficient draught without assistance; but, in the latter, this draught is increased, or produced, by bellows, or some blowing apparatus.

The employment of gas as a fuel was formerly confined to the experimental laboratory, and even here the application has increased from simple burners and blow-pipe apparatus, to the many forms of gas furnaces for melting, muffle work, &c.; but it is in large works that we have equally benefited by its introduction, and by it the highest temperatures are now obtained, equal indeed to the fusion of steel, and similar operations.

Mr. Siemens, to whom metallurgists are largely indebted for his 'regenerative' gas furnace, says that the 'advantage of employing the fuel in the manageable form of gas is that the rate of combustion may be regulated at pleasure to produce an active heating flame of any length, from little more than two feet, as in the pot steel melting furnaces, to thirty feet, as in the largest furnaces for the fusion of plate-glass; and the most intense heat may be thrown exactly upon the charge; the ends of the furnace and the apertures through which the gas and air are introduced being actually protected from the heat by the currents of unburned and comparatively cool gases blowing through them, and only mixing and burning at the very point at which the heat is required, and where it is taken up at once by the materials to be fused or heated. This is of especial importance in the case of those furnaces in which a very intense heat is employed.'*

A lamp is an instrument of common use in the laboratory, and where liquid fuel is the source of heat this fuel is so brought under the influence of a high temperature as to cause its decomposition; and the attendant flame is hence the result of the combustion of the gas generated. This is composed of hydrogen, with varying quantities of carbon, dependent upon the kind of fuel; at times, portions of carbonic oxide are also given off and burnt. Where a flame is very luminous, the gas is rich in carbon, and the luminosity is much dependent upon air being supplied just in the proper proportion to ensure its combustion, when it is thrown off as luminous particles. If, on the contrary, the air supply be insufficient, imperfect combustion is the result, and much escapes in the solid form, when we get a smoky flame which will deposit this unburned matter as soot.

Now, for heating purposes, the conditions required in this particular are much the same; for the smoky flame, from the imperfect supply of oxygen, is an evidence of the weakness of its power, and is as unfit for heating as for affording light.

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* *Chemical Journal.* New Series, vol. vi. page 208.

Hence, where we are unable to increase the draught, as in lamps with cylindrical wicks, it is better for moderate heats to employ alcohol. This gives off no unburned carbon, and affords a clear blue non-luminous flame. Oil may be used in the same way, but its flame is very smoky, and hence, except for blowpipe lamps, it is little employed in metallurgic operations, having been superseded by coal gas. Wherever coal gas can be obtained it affords a most valuable fuel, for, in the ordinary way, we can generally adjust a burner just to the point at which the air supply suffices for tolerably perfect combustion: but, of late, so many excellent arrangements have been made for mixing the gas with atmospheric air, and then burning the mixture, that such is now the common method of using it; and, indeed, by this means only we are able to obtain its maximum heating power.

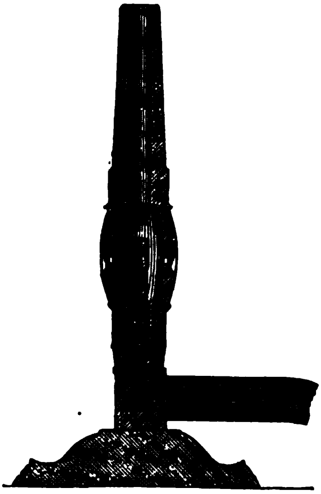

Fig. 9.

The most simple way of effecting this, upon the small scale, is by a burner known as 'Bunsen's,' now much in use in the laboratory. It consists of a tube to supply the gas, which terminates by a rather large jet, placed in the interior of a second tube, and in the smallest burners this tube would be of about half an inch diameter by five inches long, the jet opening at the lower part of this. Opposite the end of the jet, but in the outer tube, is formed a ring of rather large air-holes. These are better if provided with a sliding ring of brass (omitted in the section), in order to contract their openings as necessary. Now upon turning on a supply-cock, the gas rushes up through the outer tube from the jet, and draws in a quantity of atmospheric air by the holes in the former, which, mixing with the gas, issues by the top end. At the expiration of a moment or two it may be lighted, and the flame then regulated to a clear blue colour, by admitting more or less gas, or by cutting off the air to the requisite degree.

Thus we get a somewhat roaring flame, near the apex of which a very intense heat is afforded; so that, with the instrument here figured, a tolerably good-sized platinum crucible may be rapidly heated to bright redness. The instrument here figured is made in steatite, an incombustible mineral, which, being a very bad conductor of heat, will remain perfectly cold at its lower part, although a hot flame is burning at the top; but larger and more powerful burners are made in brass, and burners upon the same principles are now largely employed, where the mixture, instead of issuing from a single chimney, as in this case, is made to issue by a series of small holes, passing horizontally into the circumference of a hollow disc, in which the tube is made to terminate. Thus a rosette of small jets is obtained. This disc may vary in size from 1 inch to 2 or more in diameter. Again, an excellent arrangement is made on the same principles for heating a glass tube by employing a horizontal pipe, fixed in the lower part of a wedge-shaped case. The gas-delivery holes should be bored into the sides of the pipe, and the upper sharp edge of the wedge has a slit left open throughout its length. At this slit the gas mixture is inflamed, and the tube we desire to heat arranged just above the flame.

But a moderate temperature only is obtainable by a single slit. An essential condition in all these burners is that the point of combustion should be sufficiently high above the deliveries of the gas to allow the gas and atmospheric air to mix properly before combustion.

The author has for several years made much use of a larger gas furnace, made upon the Bunsen principle. It is formed of a cylinder of brass 3½ inches in diameter, and 10 inches high; this is left open at the lower end, whereon it stands, being raised from the table by three short legs. Into the upper end is driven a ring, covered with copper-wire gauze, to about ¾ of an inch down, so as to form a kind of bath, which may be compared to an ordinary sand-bath, but into which is put a number of small pieces of pumice-stone. These serve to diffuse the flame and prevent the gauze heating and burning out.

The gas is delivered from a tube placed in the bottom end, and turned up so as to deliver it at about 2 inches up the cylinder (just as in the small steatite burner); but here the air passes directly up from below, instead of through holes in the sides. A steady flame will cover the surface of the bath; but if too much gas be turned on it is apt to rise to a pointed flame, liable to smoke. While, on the other hand, for slow evaporations and the like, the proportions may be so nicely adjusted to the smallest supply of gas, that a clean crackling blue flame may be kept up all over the surface of the pumice-stone, in which any small vessel may be heated without soiling, and also free from the rising dust of a sand-bath. Then for the annealing of small masses of metal it is most useful.

But it is not only in the chemical operations of the metallurgic laboratory that gas is thus serviceable, for it is equally available in producing fusing temperatures up to that even of cast-iron; in fact, a full white heat, and the furnaces of Mr. Gore, and of Mr. C. Griffin, both answer these purposes admirably.

In both a mixture of gas and air is burned—the mixture being most effective when the proportion of air is such that it just decomposes and oxidizes the gas. This will be effected by about ten volumes of air to one volume of coal-gas; this forms an explosive mixture, and therefore one which requires management, in order to burn it quietly and continuously.

Mr. Gore's smaller furnace consists essentially of a peculiar burner, *a*. At the lower part it forms an open cylinder of two inches diameter, at the bottom of which is a pipe for the delivery of the gas, the supply of which is regulated by the tap (*b*). Closing the lower end of the cylinder is a plate (*c*), revolving on its diameter so as to act as a valve for the regulation of the air supply. The upper half of the burner is formed of a sheet of copper, corrugated so as to form a number of slits for the delivery of the gas and air mixture; this burns at the top of the burner (which tapers out to 2½ inches diameter) in numerous thin layers, with alternate layers of air between them. Mr. Gore says, 'This mode of burning the gas produces a solid flame, whilst all previous methods produced a hollow flame.'

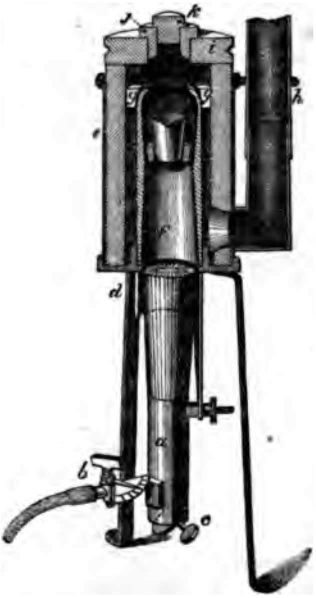

Fig. 10.

The burner, which is altogether about 1 foot long, is to be clamped under a massive iron stool (*d*), having a hole in the centre, just admitting of its entry; and above the stool is fixed the iron furnace body (*e*), lined with plumbago-ware. Its dimensions in No. 1 furnace are — height, 9½ inches; internal diameter, 4 inches; external, 6 inches.

In the centre of the body stands up a second clay cylinder, or cupola (*f*); this is held central by three clay wedges (*g*), and in its interior project three clay pieces, which are for the suspension of the crucible in the flame. A deep circular crucible is used, but in this sized furnace it must not exceed 1¾ inch external diameter. The top of the body is closed by the thick plate (*i*), having a circular opening partly closed by the perforated stopper (*j*). This second opening is entirely shut by the clay-plug (*k*). At the back and bottom of the body passes out the sheet-iron chimney (*h*), which is about 2 inches diameter by 5 to 6 feet long.

A ⅝th-inch supply is needed for the gas, and in lighting it a piece of looking-glass is placed under the burner, so that the flame is mirrored in it. The stoppers are then taken out, and a match put in, the gas being already turned fully on. The first stopper is then put in, and the air-valve adjusted. The flame is thus drawn over the edge of the cupola down to the chimney outlet. The crucible may then be put in, and the supply of gas adjusted, till a red and violet flame is got, with a little white. And this must be maintained by careful adjustment of air and gas. If the flame blows down, or is without white streaks when the gas is fully on and the air-valve open, it is an indication of deficiency of gas, and the air supply must be partly closed until the proper colour of flame is obtained.

The furnace is better used with the chimney taken loosely into a flue, in order to get rid of waste products. The bottom of the iron chimney should be very faintly red-hot in daylight; 6 ounces of copper will be melted in about 15 minutes, and 6 ounces cast-iron in about 30 minutes. Mr. Gore's No. 2 furnace will melt 50 ounces of copper, or 40 ounces cast-iron, and his large one 500 ounces silver. The Messrs. Elkington are in the habit of melting 200 ounce-pots of silver in one of these.

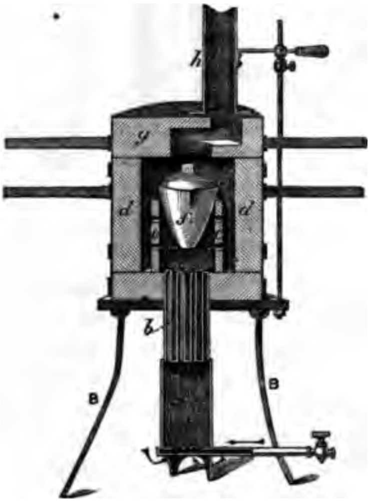

Fig. 11.

The details of Mr. C. Griffin's furnace are somewhat different. 'In his burner,' he says,* 'nothing new is offered, for it is merely a bundle of Bunsen's jets' (16 in number). And he also states that the fire-clay fittings are copied from Griffin's blast gas-furnace. Regarding the use of the burner, he says that it is necessary to supply the air certainly as rapidly as the combustion demands, yet so gradually as to avoid explosions. The first quantity is supplied at the bottom of the cylindrical burner *a*, the second at the opening, *b*, the third by just propping up the furnace body on the sole-plate by three pieces of iron of the thickness of a penny-piece; thus a small crevice is formed all round for admission of air into the flame.

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* *Journal of the Chemical Society*, Series 2, vol. viii. p. 280.

The burner (*a*) is 3 inches in diameter by 1 foot high, and the gas supply is regulated by a tap at the bottom; and as there is no air-valve, the regulation of the balance of gas to air is adjusted by the gas-tap only. An iron stool (B) is used, of such a height as that the burner, when standing on the floor or furnace-bench, just passes through it, and also through the opening in the sole-plate (*c*) placed upon this stool. The central hole in this clay sole-plate should just fit the top of the burner. Upon this plate stands a clay cylinder (*d*) 6 inches high, 8 inches in external diameter, and of 5 inches internal. In this cylinder, and surrounding the burner-hole, is placed a plumbago cylinder (*e*), pierced with holes in its sides, and adapted to support the crucible (*f*), the bottom of which is thus held up at about 1 or 1½ inch above the opening of the burner-jets. The space between the plumbago and outer clay cylinders should not exceed half an inch all round, or much heating power will be lost. On the top of the large clay cylinder is placed the dome (*g*), which is peculiar in the shape of the outlet leading to the chimney, being formed so as to turn the escaping flame twice at right angles before it passes into the chimney—an obstruction which prevents the gases passing too rapidly away from their work, and burning in the chimney instead of in the body of the furnace.

Above the dome is an iron chimney (*h*), of 2 inches diameter by 4 feet long, and hinged to a long iron arm by clamps, which admit of its being turned completely off the dome, so as to allow of the removal of the latter to get at the crucible.

Conical crucibles must be used, as they allow the flame, after striking their sides, to pass out by the holes in the plumbago cylinder; and the furnace here described admits of the use of a crucible of 4 to 4½ inches diameter, capable of holding 4 to 5 lbs. of liquid metal.

In use the gas is turned on and lighted after a short time; the crucible is then put in, and the flame regulated by its colour, as observed in the chimney, in which three holes at different heights are made for the purpose. At the two lower ones flame should be visible, but not at the top one. If it is, the gas supply should be decreased. A white heat is readily obtained, and two pounds of cast-iron may be melted, starting with a cold furnace, in seventy minutes, but, if previously heated, in forty. Four pounds will require about 2½ hours in the cold.

Silver or gold is readily and much more quickly fused in it; and for metals of low fusing point, as lead or zinc, the dome and chimney may be dispensed with.

The advantages of both Gore's and Griffin's furnaces are the capability of obtaining an intense heat without any accessory blowing. They are free from smoke and dust, are put in action immediately as required, and there is no trouble as to fuel. They each consume just about 3·3 feet of coal-gas per hour when at full work.

Griffin also converts his furnace into a muffle furnace by simply removing the cylinder D with the melting apparatus, and substituting an oval body containing a muffle. This will be again referred to in describing the dry assay of silver.

But for large and practical operations gaseous fuels are no less applicable than in the smaller ones of the laboratory; and, learning this, manufacturers now utilise the waste gases of many operations. Thus those from iron blast-furnaces are collected and applied in various ways; such, for instance, as for heating the blast itself, for puddling iron, heating steam-boilers, roasting ores, and several other uses. But the most extensive uses of gaseous fuels have arisen out of Mr. Siemens' excellent furnaces, where the gases are specially produced, and subsequently applied to their uses under the most favourable conditions.

Siemens describes his 'regenerative' furnace as consisting of two essential parts,* 'the gas-producer (Fig. 12), in which the coal or other fuel is converted into combustible gas, and the furnace with its regenerators (Fig. 13) or chambers for storing the waste heat of the flame, and giving it up to the incoming air and gas.' In the drawing (13) the arrangement is shown as applied to steel-making.

'Any combustible gas might be burned in the regenerative furnace; but ordinary lighting gas, although very successful on the small laboratory scale, is far too costly to be employed in larger furnaces; and the only gas available is that generated by the complete volatilisation of coal, wood, or other fuel, with admission of air, in a special "gas-producer." Any description of carbonaceous matter may be worked in a suitable gas-producer, and will afford gas sufficiently good for the supply of even those furnaces in which the highest heat is required. Coal is the fuel chiefly used for gas-furnaces in England.'

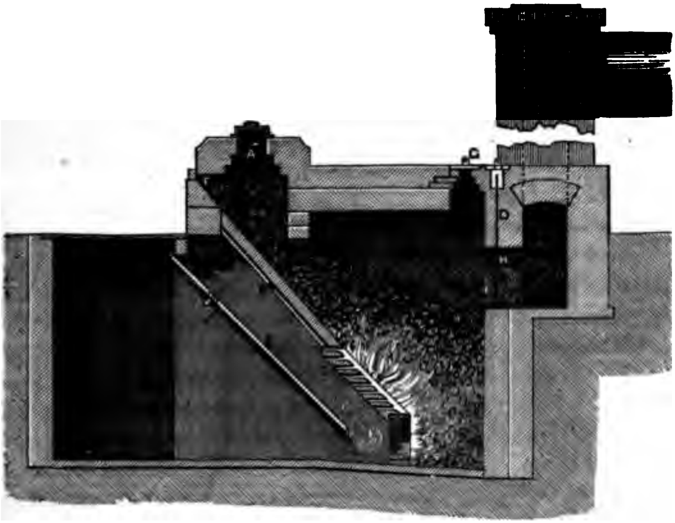

Fig. 12.

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* *Chemical Society's Journal*, New Series, vol. vi. p. 289.

The accompanying drawing is the form he gives of a producer suitable for burning non-caking slack. It is a rectangular fire-brick chamber, one side of which, B, is inclined at an angle of 45°-60°, and has a grate, C; at its lower part, and a charging-hole, A, at the top, from which the fuel falls down the inclined side on to the grate. 'Air is admitted at the grate, and, as it rises slowly through the ignited mass, the carbonic acid, first formed by the combination of the oxygen with the carbon of the fuel, takes up an additional equivalent of carbon, forming carbonic oxide, which, diluted by the inert nitrogen of the air, and by a little unreduced carbonic acid, and mixed with the gases and vapours distilled from the raw fuel during its gradual descent towards the grate, is led off by the gas-flue D to the furnace.'

A corrected analysis of the gas given by ¾-caking coal and ¼-non-caking is given as

Carbonic Oxide .	24·2 volumes.	34·6
Hydrogen . .	8·2 „	
Carburetted Hydrogen	2·2 „	
Carbonic Acid .	4·2 „	65·4
Nitrogen . .	61·2 „	
		Volumes 100·0

The gases first named, amounting to 34·6 per cent, are available as fuel. The greater part, viz. 65·4 per cent, dilutes the combustible gases.

'It is the presence of this large proportion of inert gases, which must be heated to the full temperature of the flame, that renders it so difficult to maintain a high heat by gas of this description burned in the ordinary way. In using such gas in a regenerative furnace the presence of so large an amount of nitrogen is not objectionable, as the heat it carries off is given up again to the air and gas coming in.'

Gas rises from the producer at 1000° to 1300° Fahr., and ascends to the outlet flues under slight pressure, because the gas is of less specific gravity than atmospheric air. This is maintained by mechanical means till the gas is in the regenerative furnace where it is to be burned, lest air should otherwise pass in at the various crevices of the apparatus and dilute the gas.

The producers may be at any distance from the furnaces, if only they are at a lower level; and hence Siemens says, 'It would be perfectly practicable to erect them in the mine itself, burning the slack and waste coal *in situ*, and distributing the gas by culverts to the works in the neighbourhood, instead of carrying the coal to the different works, and establishing special gas-producers at each. In rising to the mouth of the pit the gas would acquire sufficient pressure to send it through several miles of culvert.'

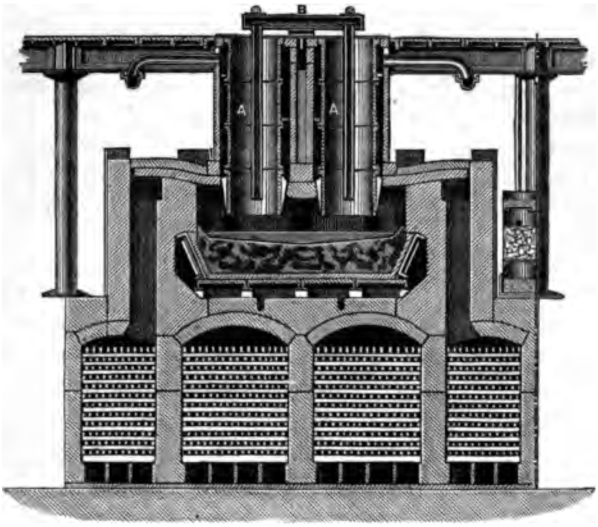

Fig. 13.

The drawing here given of a furnace for gas combustion is that of one designed by Siemens for the production of cast steel directly from the ore. The regenerative chambers are the four large arched spaces below the bed, and represented in fig. 13 as dotted, from the loose way in which the fire-bricks are stacked in them. Above these arched spaces, and below the two hoppers, A A, is the chamber in which the combustion of the heated gas takes place and the operation itself is carried on.

The gas passed in from the producers, together with the air employed, are separately heated by the waste heat of the flame in these four regenerator chambers. They are, as stated, large square spaces, in which fire-bricks are loosely stacked, so as to give a large heating surface, the amount of this surface being carefully calculated so as to balance the amount of waste heat. The waste gases from the flame ‘are drawn through two of the regenerators, and, heating the upper rows of bricks to a temperature little short of that of the furnace itself, pass successively over cooler and cooler surfaces, and escape, at length, to the chimney flue nearly cold. The current of hot gases is continued down through these two regenerators until a considerable depth of brickwork, near the top, is uniformly heated to a temperature nearly equal to that of the entering gas, the heat of the lower portion decreasing gradually downwards, at a rate depending on the velocity of the current and the size and arrangement of the bricks. The direction of the draught is then reversed, the current of flame or hot waste gases is employed to heat up the second pair of regenerators, and the gas and air entering the furnace are passed in the opposite direction through the first pair, and, coming into contact, in the first instance, with the cooler brickwork below, are gradually heated as they ascend, until, at some distance from the top, they attain a temperature nearly equal to the initial heat of the waste gases, and, passing up into the furnace, meet and at once ignite, producing a strong flame, which, after passing through the heating chamber, is drawn down through the second pair of regenerators to the chimney flue. The temperature attained by the ascending gas and air remains nearly constant, until the uppermost courses of the regenerator brickwork begin sensibly to cool; but by this time the other two regenerators are sufficiently heated, and the draught is again reversed, the stream of waste gases being turned down through the first pair of regenerators, reheating them in turn, and the gas and air which enter the furnace being passed up the second.’

By thus reversing the direction of the draught at regular intervals, nearly all the heat is retained in the furnace that would otherwise be carried off by the products of combustion, the temperature in the chimney flue rarely exceeding 300° Fahr., whatever may be the heat in the furnace. The proportion of heat carried off in an ordinary furnace by the products of combustion is generally far greater than that which can be utilised, as all the heat of the flame below the temperature of the work to be heated is absolutely lost. The economy of fuel effected in the regenerative gas furnace, by removing this source of loss and making all the heat of the waste gases, however low its intensity, contribute to raise the temperature of the flame, amounts, in average practice, to fully 50 per cent on the quantity used in an ordinary furnace; and the saving is greater, the higher the heat at which the furnace is worked. In addition to this economy in the amount of fuel used, a much cheaper quality may generally be burned in the gas-producer than could be used in a furnace working at the same heat, and in which the fuel is burned directly on the grate in the ordinary way.'

Siemens shows, in the lecture quoted, that the temperature rises after each reversal, and that 'the temperature to be attained in this way, by the gradual accumulation of heat in the furnace and in the upper part of the regenerators, appears to be quite unlimited; and the heat at which a suitably designed furnace can be worked is limited in practice only by the difficulty of finding a material sufficiently refractory of which it can be built.'

The working of the furnace is controlled by valves governing the supply of gas and air, and also by a damper in the chimney.

As to economy in working, Siemens says: 'The ordinary consumption of hard coke, costing *22s.* per ton in Sheffield, is between three and four tons per ton of steel fused; while in the gas furnace the same work may be done by the expenditure of 15 to 20 cwt. of common coal slack (worth only *5s.* to *8s.* per ton), at a cost, that is, of only *5s.* against *75s.* per ton of steel melted. There is a further saving in the number of crucibles required, as they may be used in the gas furnace four or five, and even sometimes ten times; while in furnaces heated by coke two or three casts are as much as are ever obtained. The lining of the furnace lasts at least fifteen to twenty weeks without repair (in working day and night); while four to five weeks is the longest duration of the ordinary coke-fired holes.'

At the time of giving his account of his furnace to the Chemical Society, from which I have thus so largely abstracted, Mr. Siemens had not succeeded in ascertaining the temperature arrived at with actual precision, but states that he had partly done so, viz. up to a full welding heat, which he estimates at 1600° C. = 2900° F.; and he says that, judging the heat of the steel-melting furnace by comparison of its effects, he would put it at not less than 2200° C. = 4000° F.

All the gas arrangements for heating purposes hitherto described may be called self-acting: this is to say, no means have been used to increase the heat of combustion by forcing in air; but there are many plans where intense heats are got by throwing air or oxygen into flames.

It is now rare that an experimental laboratory is formed where a supply of gas cannot be obtained; but supposing such a case, there is an instrument very useful for heating small crucibles, in which a strong blast is obtained from alcohol; so that, for operations of ignition and the like, it is all-sufficient, provided we do not require too long continuance of action.

It consists of a small double saucepan-like vessel of copper, the external case being about 4 inches high by 3 inches in diameter. The inner one is about half an inch smaller in every direction, and fixed in the outer one, so as to form an air-tight chamber between them, but provided with a tubular aperture closed by a cork, which serves as a safety-valve. From the upper part of this close chamber a tube passes down, and, turning under the bottom of the

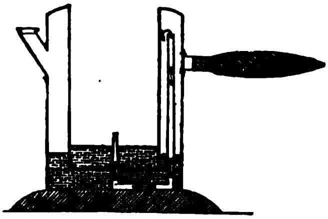

Fig. 14.

inner vessel, passes through it into the central cavity. Now, in using the instrument, about an ounce of alcohol (or more) is first put by the tubulure into the close chamber, and a similar quantity into the central cavity. When the inner is corked up, the outer is inflamed. The heat soon vaporises the enclosed spirit, whose vapour, rushing out by the jet into the midst of the inner flame, causes the latter to rise in a strong blast, capable of affording a very powerful heat.

The ordinary mouth blowpipe is a kind of miniature blast furnace. The blast is usually supplied by the lungs, and the fuel may be either a tallow candle, or be obtained by the use of a small oil lamp, or a spirit-lamp flame.

The blowpipe is most useful for small fusions, as for soldering operations, but it may also, at times, be employed for fusion of very considerable masses, up to portions of the size of a pea; and the author has seen a skilful operator fuse a farthing (a considerable weight of copper) by the blast afforded by the lungs alone, and without fatigue.

But it is for qualitative metallurgic examinations that the mouth blowpipe becomes invaluable, for by it we can command an immediate intense heat, perfectly variable at pleasure as to the nature of its action and effects, and, moreover, can work with the greatest facility and certainty upon masses of material far too minute for any other kind of manipulation; and we can, even in these small quantities, determine the various constituents of a mixed mass with accuracy and certainty.

All the best forms of blowpipes resolve themselves essentially into a tube, terminating in a fine point or jet, which latter is pierced with a carefully-shaped conical aperture; the tube itself is also provided with an enlargement, or chamber, in some part of its length, for the purpose of retaining moisture, which is always condensed from the lungs. The jet should be so pierced as to allow of just the requisite amount of air passing into the flame, and in such a direction as to ensure the most perfect combustion.

Of the many forms of blowpipe in use, probably those two known as Black's and Pepys' blowpipes are best; but of these the author prefers the former. This, when furnished with jets in platinum, forms a most effective instrument. The body of this blowpipe is simply a conical tube; to the smaller end is attached the mouthpiece, while at right angles from the side of the larger end the jet-tube passes out for about an inch, and then ends in a small platinum jet, which screws on and off. For common soldering operations this last may have a much wider aperture than ordinary; so that, in fact, the plain aperture of the tube, without any moveable jet, is all-sufficient.

Fig. 15.

On looking at the flame of a candle or lamp, it will be seen to rise conically to a point. In the interior of the cone, and taking the same form, is a smaller dark cone, *b*; indeed, the flame consists of a sheet of burning gas, which surrounds the point where it is evolved by the wick, and which flame, by so enveloping it, causes a quantity of gas to be stored from the action of the exterior air, and so to form a kind of supply chamber, as long as combustion is going on. On carefully analysing the parts of such a flame, starting from the lowest part, we may observe that, at the base of the cone, *a*, and also for a slight distance up the flame, its colour is blue, dependent upon the perfect combustion of the gas here generated by agency of the free access of air. Just at *c*, the tip of the dark inner cone, the flame is most luminous, for here particles of inflamed carbon are thrown off from the stored gas, being separated by the decomposition of some of this, under the influence of the heat of the portions burning below; and it is just in the ring of flame external to this point that we find the hottest portion of the flame, for here the air has free access to the exterior; but its heating power diminishes as we pass upwards or downwards from the point just mentioned.

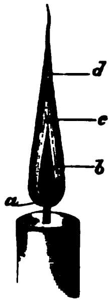

Fig. 16.

The use of the blowpipe, then, consists in throwing air into this inner cone of gas, so as to cause its free combustion, as also that of the luminous particles of carbon evolved from it; while at the same time the flame is directed by the instrument at will upon the object; but it is essential that the blast be kept steadily up, and this more particularly in quantitative or qualitative examinations with the blowpipe. Now, if we attempt, in the ordinary way, to send a strong blast by the blowpipe, the lungs will soon become fatigued: indeed, by ordinary blowing, it is impossible to keep the blast continuous, for a check will be given at each inspiration. But, if we consider the smallness of the blowpipe aperture, it will be seen that a very small blast will suffice: hence, if we can manage to keep the cheeks distended while we breathe through the nose, the natural tendency of the muscles to return to their normal state will keep up an ample blast. The mouth is replenished from time to time from the lungs, the cheeks (if at all relaxed during inspiration) being quickly restored to their state of tension.

The capability of effecting the operation may, perhaps, be acquired more readily at first by employing some solid instrument (as a pencil, for instance), and, with this between the lips, attempting to keep up a steady respiration while the cheeks are distended, breathing being carried on through the nose; then, when this can be accomplished, attempting the same with the blowpipe.

Two kinds of flame may be produced by the agency of the blowpipe, dependent on manipulation, and possessing very opposite capabilities. The first is called the oxidation flame, for any metallic bead exposed to its action (if of an oxidizable metal) will, in it, combine with oxygen of the air. It is formed by passing air just over the wick, employing for this purpose a jet with a tolerably wide opening. In this way we form a long narrow blue flame, which, if the jet be large enough and properly placed, will be quite free from yellow. Its tip is exceedingly hot, for, in addition to the blowpipe supply, it will draw a large quantity of air externally to the point: hence

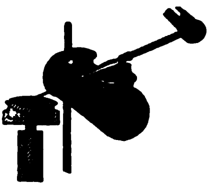

Fig. 17.

here a bead is not only immediately melted, but also oxidised, by this external air; therefore the farther it can be kept from the tip the better for oxidation, provided the heat can be maintained sufficiently.

The second kind of flame is called the reducing flame; for if a metallic oxide be immersed in such a one—that is to say, well surrounded with it—it will give up its oxygen to the flame, and the metal be reduced more or less completely. The reducing point is just beyond the tip of the inner blue cone, where there is a large supply of unburned carbon and gases, at a high temperature, consequently just in the condition to deprive any oxide of oxygen. The method of producing this flame consists in employing a rather finer jet, and at the same time placing it rather higher above the wick. Thus the dark cone of unburned gas of the ordinary flame is burned, and a small, intense heating flame obtained. In forming both oxidising and reducing flames, the wick of the lamp or candle should be well and evenly cut; and, in reductions, a support of charcoal not only assists the heating of the bead, by becoming red-hot, but also assists the action, by taking oxygen from the oxide to form carbonic acid.

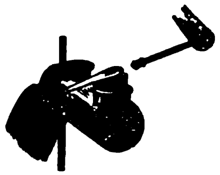

Fig. 18.

Other supports for bodies under examination are sometimes employed, as a loop of platinum wire or piece of foil, or at other times a clay basin, or a small bone-ash cupel, selected according to conditions we wish to fulfil.

The actual examination of an unknown body (after testing its fusibility, also whether it contains water, or is itself volatile) is next made in each flame, and with a system of reagents added, the most generally useful of which are borax, sodic carbonate, microcosmic salt (an ammonic and sodic double phosphate), and cobaltic nitrate.

The first, or borax, is most universally applicable, for it forms, on fusion, a clear glass, which will dissolve metallic oxides, and to which the smallest quantity, in such solution, imparts to the bead a colour peculiar to itself; the discrimination of a body, moreover, being assisted by the fact of the colour often varying in the hot and cold bead.

Sodic carbonate is effective in the reduction of metallic oxides; it is also used to test the solubility of bodies in it, and for indicating the presence of silica in combination.

Microcosmic salt, upon heating, parts with its water and ammonia, and a sodic salt containing excess of acid remains. By this change the flux is rendered capable of fusing most metallic oxides.

Cobaltic nitrate is employed mainly for the detection of alumina, and of zinc, in ores, minerals, &c.

Supposing a platinum wire be selected as a support for testing a body with borax. The method is first to heat the wire red-hot, then plunge it into the borax in powder; on again heating, the salt swells at first, and then subsides into a clean bead in the loop. It is then plunged a second time into the borax and heated, so as to increase the size of the bead; next it is just moistened by the tongue, touched on the unknown substance, and, a small quantity of the latter adhering, it is again fused until it is taken well into the substance of the bead. The heating should be first in the oxidising flame, and the peculiar reaction or changes occurring noted; it is then heated in the reducing, and careful observation made of any differences in the effect of the two flames.

In examinations with borax and other tests care should be taken not to employ too much of the substance under examination, for with borax the reaction will often produce so intense a colour as to obscure it. In such a case, however, it may often be brought out by heating the bead and then pressing it into a thinner condition or drawing it out into a thread. The intense colour being thus attenuated.

The manipulation is the same with microcosmic salt; but as the bead formed is more fluid, and therefore apt to drop from the wire, a little closer loop should be made in it, or a double loop in the form of the figure 8; and in heating a little more care must be taken to retain the bead in it. Silicates in an ore will be decomposed by this flux, the base dissolving in and colouring it; while the silicic acid forms an insoluble gelatinous mass in the substance of the bead.

With sodic carbonate a support of charcoal is generally used; and the body, mixed with the flux and damped with water, is made into a mass. Some absorption occurs in the charcoal, but under the heating, the reaction takes place all the same; yet more sodic carbonate should be added from time to time, if found needful, during the examination. The resulting bead is sometimes removed, and further examined upon platinum wire.

Charcoal supports are readily made by taking some sound small sticks of charcoal and sawing them up transversely into convenient lengths. The soundest section may then have a small cavity formed in its centre, and a carpenter's 'countersink bit' forms a handy instrument for the latter purpose.

Charcoal is most appropriate as a support in some cases of reduction with borax, rather than a platinum wire; for not only does the carbon assist reduction, but, on the other hand, if the metal under examination is reduced readily, and has any tendency to alloy with platinum, it will do so, alloying with the wire itself. Such would be the case with compounds of lead, cadmium, zinc, antimony, and some others.

With cobaltic nitrate the substance is heated in the outer flame, and most conveniently in a small pair of platinum-tipped forceps; and if a spongy piece can be selected, so much the better, as the test then permeates its texture. The cobalt solution is just dropped on it, and the change of colour observed.

For long-continued operations it is desirable not only to avoid the fatigue which is experienced by some, but also to set the hands quite at liberty. In such cases a pair of double bellows is a very useful apparatus, especially combined with the gas blowpipe, about to be described.

The author has for several years made use of a pair of square bellows, made upon the principle of organ bellows—that is, with a square underfeeder, as it is called, which may be worked by a treadle. The feeder-chamber communicates, by leather valves opening upwards only, with a large wind reservoir, which, being about 2 ft. 3 in. long by 1 ft. 4 in. wide, and rising 3 in. when full, will contain a considerable body of air. To this any pressure may be given, by placing small flat cast-iron slabs, as represented in the drawing. These are simply laid upon the upper board of the wind reservoir, and weigh 6¼ lbs. each. The pressures are calculated by the height to which the weighted bellows will raise a column of water in a glass tube. Thus, with one weight, a pressure of just one inch is obtained;

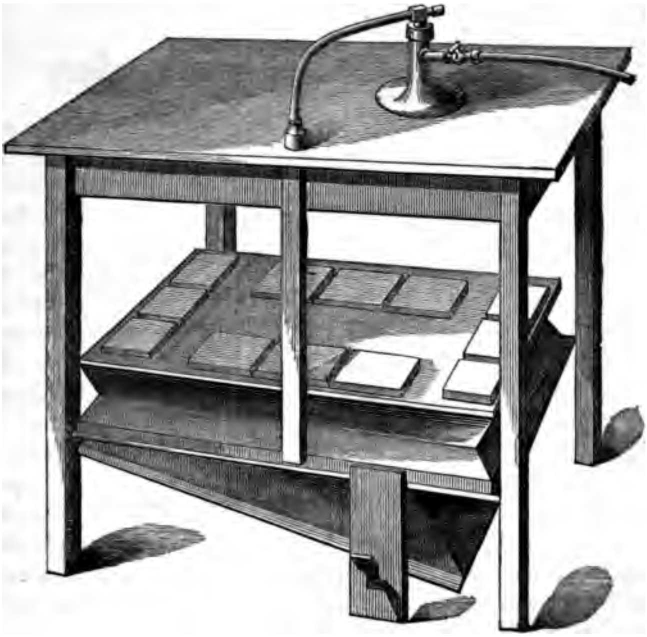

Fig. 19.

2 weights	1·7 in.	3 weights	2·2 in.
4 „	3·0 „	5 „	3·5 „
6 „	4·0 „	7 „	4·7 „
8 „	6·0 „		

These bellows are arranged between the legs of a small table, on the top of which the blowpipe apparatus can be used, the connexion to the bellows, and also to a gas supply, being made by flexible pipes.

The blowpipe alluded to, and known as Herapath's, is shown in section in the diagram, and is thus constructed:—An outer tube of brass A, ·3 of an inch diameter and 4 inches long, has a connecting piece B placed at right-angles to it, and at 1·2 inch from its outer end; by this it is screwed on to the gas tube of an ordinary burner stand. Up the centre of the tube A a second one C slides. This is 7 inches long, and ends by a smaller contracted portion, of about 1½ inch, which latter terminates in a jet. The opposite end is fitted with a piece of vulcanised tube, in order to connect it with the air-pipe of the bellows.

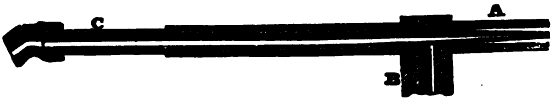

Fig. 20.

Now, as the contracted part of the tube C extends back in the outer one past the gas union, as soon as gas is turned on it passes freely to the outer end of A, enveloping the jet, and may then be lighted. Then, by putting the bellows into action, a jet of air is thrown into the very centre of the flame; when, by regulating carefully the relations of the blast and gas supply, we may get a larger or smaller flame at pleasure, and, even when applied to the more delicate operations of blowpipe analysis, a most perfect flame in its parts and effects.

In the author's laboratory (out of London, and where the day-pressure at the gasworks is always kept low) the pressure is 1½ inch; but this gives, even from a small tap and flexible pipe, more than sufficient gas for the 6-inch air-pressure, as above described. Hence the regulation of blast to flame is made by controlling the gas supply; and if the air-blast is lowered in pressure, so must the quantity of gas be diminished, and also the air-jet be passed nearer to the mouth of the blowpipe. These points should be so nicely adjusted as to obtain a clear, blue, horizontal flame, without any red rising from its commencement.

For qualitative analysis by this blowpipe, two of the weights, with a corresponding small proportion of gas, give a very efficient flame; but for some fusions more gas, with more air-pressure, may be needed.

Now the oxyhydrogen blowpipe is just this apparatus, differing only in scale, and in the inner or jet-tube carrying pure oxygen in place of air. By this the most intense heat obtainable by chemical means is got, especially when the combustible gas is pure hydrogen. Indeed, Deville fuses large masses of platinum and other infusible metals readily by it. As an example of its powers, Messrs. Johnson and Matthey had, in the Exhibition of 1862, an ingot of platinum they had so fused and cast, of 2½ cwt.; also a cake of iridium of 27½ oz.; and they ran 1 oz. of rhodium into a button by its means.

A large application, or rather extension, of this apparatus has been contrived and perfected by Mr. Griffin, under the name of Griffin's patent portable blast-furnace; and although he has rather set it aside for his gas melting furnace, already described, in consequence of its requiring constant bellows-working, it may yet be briefly described here. It consists essentially of a series of these jets, in his small furnace amounting to 6, in the medium to 16; and in a large one which he supplies their number is increased to 30; although, for the latter, the supply of gas required is so large as to limit its usefulness to some extent. The gas is supplied to a burner in the form of a cylindrical turned iron box, from the upper surface of which it burns from circular holes. In the centre of each of these is a jet in connexion with an under chamber, into which air is forced from a pair of double bellows, and at a pressure of 5 inches; that is to say, the pressure is capable of sustaining a column of water 5 inches high. The supply of gas afforded by a half-inch pipe suffices for the medium burner. The burner is arranged in a fire-clay furnace, and placed either above and inverted, as in the drawing, so that the flame may play down upon the pot; or it may be placed below, so as to act on its under side.

The pot itself is surrounded by a small perforated jacket, and placed at a proper distance from the burner, viz. at about 2 inches from it. Between the jacket and outer wall a quantity of small pebbles are put, so as to retard the heat in its passage outwards; and these are said by the inventor to be indispensable, where the extreme effects of the furnace are desired.

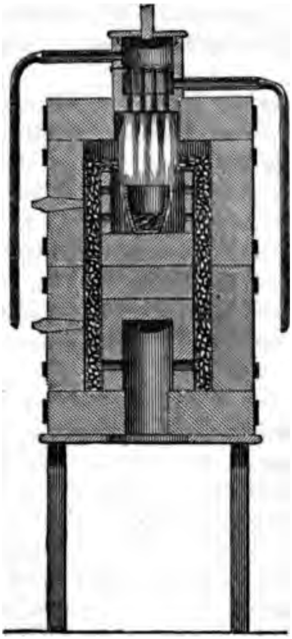

Fig. 21.

Mr. Griffin says that quantities of 8 to 10 pounds of copper were melted into a homogeneous mass, with a 16-hole burner, and half-inch gas-pipe, in one hour. 45 ounces of nickel were fused; 18, 28, and 40 ounces cast-iron were tried; 18 ounces fused in 1½–2 hours. The 40-oz. crucible gave way just before fusion.

The furnaces for solid fuels, and employed in metallurgic operations upon the small or large scale, may also be classed under two kinds, viz. wind and blast furnaces. The first comprising all those wherein the draught is created by natural means only, and especially by the careful proportioning of the size of the furnace, and its arrangement of air, draught, &c., to the size and height of the chimney; the second, those where the heat is urged by throwing in a powerful blast from some blowing-machine, so that the flue is a secondary matter, if needed at all.

For the melting of gold and silver, as for all ordinary melting operations, the common form of wind furnace is usually employed. An essential part in it is a brick chimney, sufficiently high, straight, and somewhat gathered in at the top. This may be built in a wall, and the furnace placed at bottom, in the front of it; and, for operations of moderate extent, an ordinary house-flue will often suffice. The most effective height for such a chimney is found to be about 30 times the diameter of the furnace built to it. The author constructed an excellent one in his own laboratory some years since, upon the following plan and proportions. The chimney was just 30 feet high and 1 foot in diameter; upon the face of this the furnace was built, the ash-pit being upon the floor level; but, where heavy pots have to be lifted out and in, it is sometimes preferable to sink it somewhat, and, moreover, by so doing, the ashes are prevented from falling out into the laboratory, being retained in the so-formed pit.

The lower part of the furnace was carried up solidly in good bricks and coal-ash mortar for 1 foot 6 inches, the centre space being about 13 inches square, and the walls 9 inches thick. At this height a bar was placed at back, 1 inch in width, and 1½ inch deep, running from side to side, with a similar one in front. These were for supporting the fire-bars, which latter were of wrought-iron, each bar being 1¼ inch deep, 1 inch broad at the upper, and ½ inch at the under surface. Each end was flattened out ¼ inch on each side; thus, when laid together, ½-inch spaces were left at the top, gradually opening out to 1 inch underneath. Above the fire-bars the furnace was carried up to a height of 1 foot 10 inches in the front, the sides being sloped up to the back wall, which was 2 feet 3 inches. This latter portion, or fire-chamber, was solidly built in Stourbridge bricks, the joints being very small, and made in good, well-tempered fire lute. At the top an iron ring was worked in, the ends being crooked into the chimney, so as to tie all together. This ring was formed of iron 2½ inches broad by ¼ inch thick.

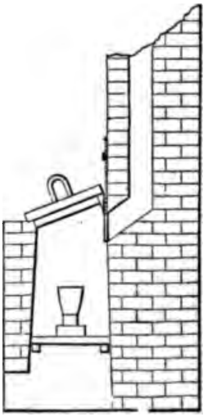

Fig. 22.

If such a furnace is likely to be subject to much wear, it is better to cover the top round the brick-work with a cap cast stoutly in iron. This forms a smooth, clean opening round the fire-pot, and saves wear of the brick-work. The furnace just described was drawn in gradually from 13 in. at the fire-bars to 11½ at the top. Thus increased space was afforded at the fire-bars for fuel, and at the same time the taper walls exercised a kind of reverberating effect upon the heat.

At about 7 inches from the top, the flue passing into the chimney was carried out, and at an upward angle, so as to free it from sharp turns, which would check the draught. And here the damper was built in so as to drop by a chain, and close the chimney opening; the body of the furnace being also capable of being closed up by a large Stourbridge tile, mounted with a rim and handles, so as to slide and cover the fire-pot closely when the furnace is in use.

As a rule, it is better to use as little as possible of iron in the way of ties and straps in furnace-work, as its expansion and contraction being so different from the body of furnace material, it is likely to cause cracks and unsoundness in the work, especially if injudiciously placed.

At Messrs. Browne and Wingrove's, the Bank melters, where large operations have to be performed with much speed, twenty-four of these furnaces are built in one large room, being placed in four divisions of six each in each angle of the room, that is, three upon each side wall; the centre of each wall having a door opening to admit air. The coke is stored in the centre of the room so as to be accessible. These furnaces being frequently employed for melting silver bars of 2000 or more ounces each, are lowered so much that the top opening is not more than about 1 foot 8 inches from the ground, hence the lifting of a heavy pot is facilitated. Again, the tops are closed by a couple of thick iron plates, which, sliding on an iron fillet placed on the top, admit thus of the quick opening and closing of the furnace. It is always advantageous to have a small door, opening on each side of a wind-furnace at the fire-bar level, wide enough to expose the ends of at least two bars on each side. By these openings we are able to withdraw the bars, and allow the fuel to fall into the ash-pit, and so lower the heat immediately, a proceeding sometimes desirable. The crucible remains standing upon the centre bars.

As a construction of furnace known as the reverberatory furnace will frequently be mentioned in the special part of this book, it may as well be described generally here, bearing in mind that it is constantly modified to suit particular operations.

The characteristic point in the reverberatory furnace is, that the fire-chamber (A) is separated from the one in which the material to be operated upon is placed, and the general construction is such that the heat and flame may be thrown down upon the charge. This fire-chamber is built up solidly in front; immediately behind this, and rising somewhat above the level of the fuel, is formed a bridge, or wall of fire-brick (B), in some cases built to a thickness of 2 feet, and then carried full a foot high above all.

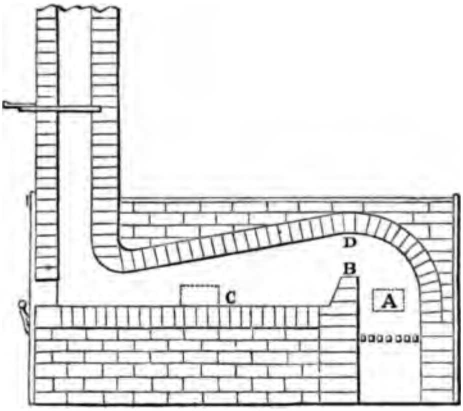

Fig. 23.

Next, passing backwards is the sole or bed of the furnace (C), variously formed and proportioned, according to the kind of work to be performed in it. Thus, in the furnaces where the first operations upon copper ores are carried out, they are flat and shallow, for the object here is to expose a large surface to heat and air, so as to drive off sulphur and absorb oxygen. In others, a depression is formed in the sole itself, so as to allow of the gravitation and collection of fused matters; but in all cases, as the load to be sustained is more or less considerable, so this part of the work is very compactly built.

Rising from the front wall above the fire-pot, and passing backwards, is the reverberating arch, D; this rises so as to be from 1 foot to 18 inches above the bridge as it passes over, from which elevation it is made to descend gradually to the back of the sole, where it ends in a chimney, seldom less than 40 feet high, as it is always carried sufficiently high to cause a strong draught.

The height of the reverberatory arch above the bed also varies according to the different uses of the furnaces. Thus, in some, where working upon the contents of the bed has to be carried on, they are kept high; while in others, as in lead-improving furnaces, the arch is carried low over the bed so as to bring the heated currents of air as much as possible in contact with the fused metal.

Now it will at once be seen that the body of heat and flame passing up from the fire is at once thrown back, or, as it is said, 'reverberated,' by the formation of this arch immediately above, and inclining towards the back, where the chimney vent is situated.

In large reverberatories, openings are formed at the sides as the working may require. Thus, in those employed for cupelling silver upon the large scale, it is not only necessary to be able to inspect the operation, but also to form an entry for the bellows blast, and beside these, outlets for the litharge generated. Again, in iron puddling furnaces, which are of this class, the operation is effected by a workman using a paddle through a side door, opening at about the centre of the sole of the furnace.

It may be mentioned that here, this general description of these furnaces may suffice, as they are almost entirely employed in large operations; the muffle furnace supplying their place for small ones. This latter will be described when the subject of the assay of silver and gold is treated of.

Passing now to blast-furnaces, the ordinary blacksmith's forge may be given as an instance of the most common form, as well as an illustration of the principle. In it an intense and concentrated heat is produced by a very small amount of fuel. Indeed, in blast-furnaces generally (if we except the large blast iron furnaces), the fire-chamber would, at first sight, appear to be very inadequate to the great heat obtained, but it must be remembered that (as in the blowpipe) this depends upon the amount of oxygen thrown in by the blast, whence also the heat is rapidly got up.

Two forms of these furnaces may be described here as particularly useful in the laboratory for small melting operations, and the like. The first is one described by Faraday in his 'Chemical Manipulation,' to which the reader is referred for its more particular description. It is formed of a large black-lead pot, in which is placed a second smaller one, the space between the two being filled with pounded fragments of old pots. The bottom of the inner one is sawn off so as to admit of the grate being placed inside it, to form the fire-chamber. The bellows nose is admitted by a hole bored through the outer one at its lower end. As a fuel Faraday employed coke, and he says, that compared to the heat obtained its consumption is very small, and, further, that the want of vessels which will withstand the intensity of the heat produced has hitherto been a limiting cause to its usefulness. It is, nevertheless, a most useful and effective furnace, and very portable and manageable. The furnace known as Aikin's blast-furnace is formed somewhat in the same way.

The second form is that known as Sefstrom's furnace, which I have long been in the habit of using, and which is a most effective apparatus. In its construction two cylindrical vessels are first formed in very stout sheet-iron; the larger, which is to form the outer wall of the furnace, may be 8 inches high by 9 inches diameter. The smaller or inner vessel should then be the same height, but of 7 inches diameter; upon the outside of the latter are fixed six small iron squares, three at the bottom by way of legs, and the remaining three at equal distances round the circumference; and at 1½ inch from the top, these serve, when the small vessel is in its place in the larger one, to keep the two apart, so as to leave an air-chamber, 1 inch wide, between them both at the sides and bottom. A sheet-iron ring is formed just to fill up this space between them: this is dropped upon the three side squares, and the little gutter so formed is next plastered up by lute. At the bottom of the outer vessel a taper tube is fixed, of about 1 inch in diameter at its smaller and outer end. This is for connexion with a pair of table bellows, by which the blast of air is to be supplied. Then in the inner chamber eight holes of ¼-inch diameter are formed; and at 3 inches from the bottom, these give passage for the blast to the fuel, all around the crucible. The fire-chamber is lined by fire-lute to about ¾ of an inch in thickness, both upon the bottom and round the sides; and its capacity is increased by a ring of sheet-iron, two or three inches deep, made to slip over that part of the inner vessel which stands above the outer one; thus increased depth is given for fuel.*

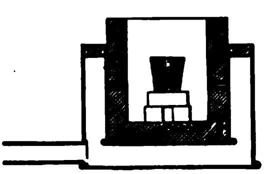

Fig. 24.

In using this furnace, an inverted pot may first be put in to serve as a stand for the crucible, so as to bring its bottom part about up to the level of the air-holes. The fuel is then thrown in to the same level, and the crucible put in; next a little hot charcoal, when the whole is to be filled round the crucible with anthracite. In such a manner the author has melted a bar of silver of two pounds weight in about fourteen minutes from the time of putting it cold into the pot; but it is necessary to have the fuel first of a fit size, neither too large, nor containing any dust, and also to keep the blast steadily up from the bellows. On the whole, it is a most useful furnace, and operations may be carried on upon a tolerably large scale in it. The dimensions given here being for a very small one. Indeed this size may be well used upon a stool placed upon the bellows table described at page 89. Its disadvantages, however, are the need of effective solid fuel, its needing a blast; and last, but not the least, the dust that is thrown out from it in use. Hence where gas can be obtained, one of the gas furnaces on the wind plan already described is to be preferred.

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* Both this ring and the squares are omitted in the drawing.

In the 'An. de Chem. et Phys.' for 1856, Deville describes a most powerful blast-furnace on a somewhat similar plan to Sefstrom's. It consists of a cylindrical iron vessel, having a hemispherical bottom. It is lined with fire-clay, and the bottom is covered with a circular plate pierced with holes through which the blast is thrown up. The heat so obtained is, with proper fuel, intense. Deville melts platinum in it, and states that it runs down ordinary crucibles, so that he employs lime ones, or at times, carbon or alumina crucibles. One advantage of his form of furnace is the capability it affords of much more easily removing ash and clinkers.

For the construction of furnaces a class of clays are employed, known as refractory or fire-clays. These are used not only in furnace-building, as mortars are in usual building operations, but also for the formation of fire-bricks and lumps, and further, for the fabrication of various vessels and apparatus required to stand extreme heats such as crucibles, muffles, retorts, and the like.

Speaking generally of clays, they are composed of alumina, silica, and water; when comparatively pure they are nearly white, but they are generally associated with other bodies, which modify their appearance and properties. Thus they frequently contain lime, magnesia, and oxide of iron. When heated, their water is driven off, and then they shrink considerably, as in the burning of ordinary bricks for example. If strongly heated, partial fusion takes place. Thus in some kinds of pottery the glazed surface is a fused one, and again the clinkering of bricks is an example of the same fusion.

The plastic paste obtained by moistening clays with water, is very tenacious, and hence capable of being moulded into various forms, which are maintained after drying and burning; although somewhat contracted from loss of water and shrinking, as above stated.

The essentials of a good fire-clay are:—That it should be thoroughly refractory and infusible;. so that from the former quality it shall stand exposure to rapid changes of temperature without cracking, and from the latter, high heats without any great degree of softening, and consequent alteration of shape. The greater the amount of silica in them the better for these qualities, and thus, where a clay is deficient in silica, it is customary to add sand in working it.

On the other hand, any considerable quantity of lime, magnesia, or oxide of iron, tends much to render a clay fusible. Fusibility varies also with the porosity of a clay after it has been burned, and also with the method itself of burning. Their contraction is influenced by the amount of water they contain, therefore for lutes, as also for material for crucible-making, it is always necessary to work with the raw a certain quantity of old burned clay, either grinding for the purpose broken crucibles, portions of old ones clean from any substances for which they may have been previously employed, or else fresh clay burned for the express purpose, so as to have at least one-third of the mass made up of such dehydrated material; and it is for the same object that sand, graphite (carbide of iron), or powdered coke, are also so mixed.

The clays are found in many parts of England, but by far the greatest amounts are from Stourbridge and Newcastle.

The following table, containing some analyses of Stourbridge and Newcastle clays, will give the reader a clue to the relative proportions of the chief constituents:—

	Stourbridge analyzed by Berthier.	1st Variety of Newcastle Richardson	2nd Variety of Newcastle Richardson.	Average of 7 Varieties of Newcastle Richardson.
Silica . . .	63·70	83·29	47·55	60·30
Alumina . . .	20·70	8·10	29·50	23·61
Oxide of Iron . .	4·00	1·88	9·13	4·11
Lime and Magnesia .	...	2·99	2·05	2·59
Water . . .	10·30	3·64	12·01	9·1

An analysis made in my laboratory of Stourbridge clay, by Cowper, gives very closely the same composition.

It will be seen that, in the two single analyses of Newcastle clay, great difference as to the proportions of silica, alumina, and oxide of iron exists, and, consequently, corresponding difference in their characteristics in use; but in the last column, where an average of seven varieties is given, it will be observed that, upon the whole, their proportions very much assimilate those of the Stourbridge clay, and that in them the proportion of silica is very large, hence their refractory nature; and an extreme point as to the proportion of silica is reached in Welsh Dinas clay, which Percy speaks of as Dinas material, which 'is called clay,' and gives the following analysis of it:[*] Silica 98·31, alumina 0·72, oxide of iron 0·18, lime 0·22, potash and soda 0·14, combined water 0·35, = 99·92 parts. For working, it is mixed with 1 per cent lime, and sufficient water to form a paste.

Siemens says that Welsh Dinas brick is the only material practically available on the large scale which he has found capable of resisting the extreme heat of steel melting furnaces, and that it is 'nearly pure silica.'

Nearly approaching the latter in the quantity of silica is the clay found at Ewell, in Surrey. This latter, as also the 'Windsor' clay found near Hedgerley, in Bucks, has been much used by the author and found excellent. Riley[*] states that the bricks made from Ewell clay contain 91·84 per cent silica. The clay itself is of a greenish yellow colour, and very plastic. The latter authority states the amount of silica in Dinas brick as 94·33 per cent. Cowper's analysis of the Monmouth clay gives 75·3 per cent silica, and of Pembroke 88 per cent.

Lutes are a class of cements formed for the most part of refractory clays. Thus, when employed as a mortar in furnace-work, they give the finished work a homogeneous structure. They are also used to cement the joints of apparatus, as covers upon crucibles, the junctions of tubes, the fitting up of muffle-work, and the like.

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[*] *Metallurgy*, vol. i. p. 237. [+] *Chem. Soc. Journal*, 1862, vol. xv. p. 322.

Stourbridge clay forms by far the most applicable lute, and when ground up with a portion of previously burnt clay, or broken crucible ware, as described, it will resist high temperature better than any other material. In using it, the powder should be moistened with water, allowed to soak a little time, and then well beaten with a heavy wooden mallet until quite plastic, and in that state it should be employed.

Ewell clay, or again Windsor loam, may be thus used. The latter, as already stated, is a natural mixture of clay and sand, and serves well, when applied as a coat to clay vessels, to diminish their porosity. For this end it should be mixed with a tenth part of borax, and the mixture made tolerably thin with water, so as to apply it with a brush.

There is also a lute much used for the latter purpose under the name of 'Willis's lute.' It is made by dissolving 1 oz. of borax in half-a-pint of water, and then adding slaked lime enough to form a thin paste; this is brushed over the vessel and allowed to dry. Then, before using, a second coat of slaked lime in linseed oil is applied. This latter should be of the consistence of a plastic mass. The vessel is then allowed to dry for two or three days, when the pores will be found to have been thoroughly closed up if the application has been carefully made.

F. B. Miller similarly employs borax, but alone, in order to do away with the porosity of a clay crucible; he dips it in a saturated hot solution, and by this means so fills the pores, as to render it impervious to even so fluid a body as fused argentic chloride.

In some of the more delicate operations of the metallurgic laboratory, glass tubes are employed; and it is often necessary to secure any junctions by the aid of lute; now for such purpose plaster of Paris forms an excellent one, especially if mixed with glue-water, when it will dry and form a very firm joint. The secret in using plaster of Paris consists in making it sufficiently thin, and applying it quickly. The glue causes it to dry slower and assists in forming the joint.

In building large furnaces such as those for reducing iron ores, as blast furnaces and similar large works, a brick is employed formed from Stourbridge or some analogous clay, according to locality, but, in the construction of the small furnaces of the laboratory or melting-house, two kinds of bricks are employed under the name of fire-bricks, for in all cases the ordinary building bricks are quite unfitted for such purposes, the clay of which they are formed contains too much alumina, and is too much mixed with foreign matters (as oxide of iron and the like) to resist the action of the fire, as also to sustain changes of temperature; consequently they would be speedily cracked and broken up by such use, if at all exposed to heat, and therefore, where we are compelled to employ them, it should only be for external work; the fire-chamber in such a case being lined with Stourbridge bricks, or fire-lumps. The analysis of an ordinary sample of building brick clay may be here given as an average example: silica 49·44, alumina 34·26, oxide of iron 7·74, lime 1·48, magnesia 5·14, water 1·94 = 100 parts. Stourbridge clay forms most refractory bricks. They are white, dense, and compact, and most valuable for all large kinds of work, where there is not much shaping or cutting required. But in the smaller kinds of furnace work, where consequently some cutting has to be done, it is only to be effected by carefully operating upon them with the chisel and hammer.

Hence for such small work the second kind of bricks known as Windsor, or in the trade PP bricks, are very useful. These are not much known, as their manufacture is confined to Hedgerley, a small place near Windsor. They are of a red colour, very silicious, but soft, easily cut and shaped, and yet standing heat very well. The best method of cutting them is by a piece of zinc roughly notched out as a saw, and then the more accurate figure required may be readily given them by grinding upon a rough flat stone. In this way the small circular furnace formerly made by the late Mr. Newman, and sold by him as his 'universal furnace,' was lined by cutting the bricks with care to the radius of the circle they are to form, when they key in like an arch, and so need no luting whatever. And any similar small work may be thus compactly lined with them, without lute.

For the formation of crucibles there is no material equal to such clays as contain little or no lime or oxide of iron. But crucibles formed even of the best varieties of clay are more or less fusible under strong heats, especially when used with certain fluxes, which are liable to act upon them, but by well working up with the clay a portion of carbide of iron or graphite, their infusibility is much increased. Crucibles containing this addition are known as black-lead or plumbago crucibles. Their capacity for resisting changes of temperature is also increased by this mixture, even as by that of sand, flint, or ground-up pots, as before mentioned; but all these qualities are far best obtained by means of graphite in moderate quantity; if, however, it bears too great proportion, it is liable to burn out and leave a porous crucible. The mixture should not exceed two to three parts of black lead to one of clay, according to circumstances.

But, although excellent in the above desirable qualities, there are cases wherein we cannot employ black-lead pots; for instance, metallic oxides, if heated in them, are sure to be partially reduced, and in some cases completely, consequently in such cases we are thrown back upon the ordinary clay crucible. At Krupp's works at Essen, where immense quantities of steel are melted for the same cast, black-lead crucibles are used, and but for one operation, after which they are ground up, mixed with fresh material, and again formed into pots for further use.

In the manufacture of crucibles, the clay, after being exposed to the air, or weathered (and this is best done in winter time, when water and frost disintegrate the clay), it is ground, and then treated with water; and if black-lead crucibles are to be made, this substance is mixed with the material. As their excellence much depends upon thorough incorporation of these matters, the mass is next well worked up in a mill, or, in some places, it is trodden for some hours by the feet, until it becomes thoroughly plastic. It is then formed into crucibles upon an ordinary potter's wheel, after which they are dried slowly and burned.

Three kinds are in common use, the Hessian, or triangular, Cornish, and London pots.

The first are of a coarse brown clay, which contains a good proportion of sharp quartz sand, they bear a very high temperature without getting out of shape, nor are they very readily acted upon by fluxes.

I have used these pots and found them very good, but Percy says that those he has tried do not justify the high character to which 'the genuine' he has no doubt is entitled. He says they were too readily acted upon by oxide of lead, and this, by the way, is a fault of all pots made of very silicious clays. The Hessian pots are made of Almerode clay mixed with its own weight of sand. Berthier gives their analysis as 70·9 silica, 24·8 alumina, 3·8 sesquioxide of iron, = 99·5 parts. The Cornish pots are nearly white, and of a rough texture; they are excellent in quality, more especially the small pots. I have used those made by Juleff (of Redruth); these have been analyzed by Dick, and very much resemble in composition the Hessian in their relative proportions of silica and alumina. They contain 72·39 silica, 25·32 alumina, 1·07 sesquioxide of iron, 0·38 lime, a trace of magnesia, and 1·14 potass, = 100·30 parts.* The London pots are neater and more cleanly in appearance, but are the worst in quality, being very readily softened, and, moreover, the large pots not capable of standing changes of temperature without cracking. They are reddish-brown in colour. Smaller pots are made of a white clay by the Plumbago Crucible Company under the name of white fluxing pots. I have used the smallest of these as annealing pots. These stand moderate temperatures well, and rapid changes without cracking.

An excellent small pot is imported from France for annealing operations in gold assaying, but the French also make good refractory crucibles for general use; they are known as Beaufay's, and as Deyeux's crucibles. The latter are very refractory, and, like the Hessian, are formed by mixing clay and quartz. They contain 72·3 silica, 19·5 alumina, 3·9 sesquioxide of iron, and 1·8 water, = 97·5 parts.

Beaufay's are composed of 1 part Ardennes clay as found, and 2 parts of the same burned, ground, and worked with the former.

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* Percy, *Metallurgy*, vol. i. p. 222.

Composition, 64·6 silica, 34·4 alumina, 1·0 sesquioxide of iron, = 100 parts.

Of all fluxes there is none so destructive to clay crucibles as litharge, it will corrode and eat completely through them by forming fusible compounds with the silicates of the clay; but the alkalis, or calcareous matters contained in the ash of the fuel employed, also act as a corrosive flux upon them. Hence, we sometimes enclose a crucible in a second one, with a layer of clay between them, when employed under such circumstances.

It is also customary to line a crucible where we fear it may be acted upon by its contents, or where it is an object to prevent their adhesion to it; or at other times this is done to furnish carbon to metallic oxides to be heated and so decomposed. For these purposes, charcoal is employed, and in the following manner:—The crucible is first wetted; then a paste of powdered charcoal with water is pressed on to about half an inch thick with a wooden pestle; after slightly roughening this, a second is applied; and again until the pot is full. Then the centre is scooped out as much as requisite, and it may be to within half an inch of the bottom, and a quarter or less at the sides, the surface being at last left quite smooth by burnishing. Where such treatment is inapplicable, as in some cases where litharge is employed, the action of the latter may be much diminished by rubbing the pot well over with red ochre, or even with chalk.

Percy gives the following method of 'brasquing,' or lining crucibles with charcoal for purposes of iron assaying, where small No. 1 French crucibles have to be so lined:—Mix 6½ oz. charcoal in powder with 1 oz. 5 dwts. of treacle, and beat it in a mortar with enough water to make it cohere. The crucibles are then lined (and the above quantity will line about two dozen such as named), and the cavity pressed out by a former. They are then covered lightly, put into a muffle, and heated till flame cease to appear at the mouth, and removed when cold. He says the lining should be smooth, with no cracks, and close in texture.

In order to ascertain the qualities of crucibles, the following tests may be employed:—

First, if they are ordinary clay ones, they are to be heated intensely and then exposed to sudden cold by withdrawing quickly from the furnace; if they stand this it will be as much as can be expected from them. But, in the case of black-lead pots, they should be capable of bearing the sudden plunge into a vessel of cold water at the moment they are withdrawn from a hot furnace, the pot being of a full red heat when plunged in.

I constantly test them in this latter way, and remember first seeing Mr. Ruel, some years since at his factory at Shepherd's Bush, make a large pot (capable of containing some ten or twelve pounds of melted metal), nearly white hot, and then plunge it into water as removed from the fire. This it stood without cracking or the least injury.*

Secondly, they should be examined as to their fusibility, by taking a small fragment, and heating intensely before the blowpipe; if the ragged edge remain so, without rounding from fusion, the pot is perfect in this respect.

Then they should have a quantity of litharge fused in them, many will be quite destroyed, and the litharge pass through holes formed in them by its corrosive action, others will be more or less softened by this test.

Lastly, the closeness of their texture is shown by the time elapsing, after filling them with water, before it appears externally. Sometimes, however, they are made purposely porous, as in the case of assay pots, where metal is first introduced into the pot with water, the last portions of which have to be driven out during the annealing of the metal.

Crucibles are sometimes formed of iron; thus, in our Mint, all the silver for coinage was, until lately, melted in iron pots. They now employ plumbago. Their use, however, is more fit for saline fusions in the laboratory. Crucibles are also made of fine porcelain, of gold, of silver, and of platinum, according to desired uses; the latter being invaluable in the laboratory of research, from their power of resisting chemical action, and also from their excellent conduction of heat, by virtue of which they become speedily and uniformly heated, even in some cases in the ordinary gas flames already described.

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* Messrs. Ruel's pots are excellent in quality, as also are those of the Patent Plumbago Crucible Company at Battersea.

CHAPTER V.

OF THE FUELS APPLICABLE TO METALLURGIC OPERATIONS.

In considering the various fuels applicable to metallurgic operations, coal may occupy the first place, as being, in this country, of by far the largest application, either in its raw state or prepared as coke. The first is useful where a flaming fire is required. This flame is the result of the evolution of combustible gases, which also render coal easy of ignition, for the first application of heat to it causes their evolution and ignition, and they assist in inflaming the actual carbon of the coal. Hence a carbonaceous coal like anthracite, which contains little or no gas, is difficult of inflammation, and this is further increased by its density, for charcoal, also nearly pure carbon, inflames readily, because its porous, or non-dense condition, allows of its retaining much atmospheric air, which facilitates its combustion.

In coke we have a fuel which burns with a bright glowing heat and no flame, for the latter is always due to combustible gases, and these have been slowly distilled off, in forming the coke. Coal may be called mineralised vegetable matter, which, during the change, has been compressed, and also altered in its chemical properties, its vegetable origin being completely proved by microscopic examination. It contains, also, varying quantities of earthy and inorganic substances, and occurs in seams of thickness ranging from half an inch to three or four feet, the seams being always separated by corresponding ones of true mineral matters, such seams being called partings. What are popularly known as slates in coal are only portions of this mineral matter.

The appearance of coal varies much; in some the surface is dull, as in cannel coal; in others, as some anthracites, we have a bright glossy surface, with almost metallic lustre. Some coals break up in conchoidal masses, others exhibit a tendency to crystalline structure. The specific gravities also vary much, ranging from 1·00 to 2·00.

When distilled in close vessels, coal gives three classes of products. First, gaseous, consisting of compounds of carbon and hydrogen. Secondly, liquid, as tar, ammoniacal liquor, and other similarly constituted bodies. Thirdly, as a residuary product, carbon, with the earthy matters originally present.

Coal may be classed under six varieties. The first, that in which the coal transformation is least complete, as in brown Devon coal, where the strongly-marked remains of vegetable origin have given it the name of 'Lignite.' And evidence of its retaining its woody or vegetable fibre is given in the fact of the capability of distilling acetic acid from it. Indeed it may justly be called fossil wood. Its specific gravity is about 1·5.

Second, the Cherry, or Staffordshire coal, which gives a sparkling yellow flaming fire, but which consumes rapidly. It does not cake. Specific gravity, 1·28.

Third, the Hard, or Splint coal of the Glasgow iron district, so called from its splintery fracture. It gives a very strong heat and clear fire. It approaches the next variety, or Cannel, in character. Specific gravity, 1·305.

Fourth, Cannel coal; a clean coal on the surface, so much so as to be wrought like wood into ornamental articles. Its fracture is often conchoidal, and colour varies from brownish to jet-black. It is an excellent gas-producing coal, and burns with a clear crackling flame, whence it is sometimes called Parrot coal. Specific gravity, 1·318.

Fifth, the ordinary Newcastle or caking coal. This abounds in bituminous matter, and consequently, when heated after splitting up, cakes together and gives off bubbles of gas. This property renders it, if used alone, very unfit for metallurgic operations, by rendering good access of air impossible, and hence high temperature unattainable by its use.

But caking coal is sometimes added to non-caking in small quantities for metallurgic work. The specific gravity of Newcastle coal is 1·3.

Sixth, anthracite, which for furnace operations is a most useful coal. It is quite free from bituminous matter, and, when in its true state, contains carbon, inorganic salts, and water only; but generally, not being quite true, hydrogen and oxygen are found in it. When any bitumen is present, it is called semi-anthracite. Its texture is very hard and compact, being the densest coal known; it is jet-black, and very brittle; and as it encloses water in its substance, it readily splits and breaks up under heat. It is the chief coal of America, and largely used there in ironworks, its pure carbonaceous character producing first-class quality of iron. In Great Britain it is found chiefly in the South Wales fields; also in Staffordshire, at Walsall. Its density renders it very difficult to light, and it can only be burned where there is a strong draught; but at the same time there is no fuel which, for the same bulk, affords such a powerful heat. Hence, for assaying operations, it is invaluable. Its specific gravity is 1·36.

About 10 per cent of pit coal is made up of ash. This ash is composed of alumina, iron, lime, traces of magnesia; and with these are associated sulphuric and phosphoric acids, but no alkalis are found in it. Iron is also associated with coal in the form of iron pyrites, a bisulphide of iron; and this is a very noxious constituent where coal has to be employed in metallurgic or manufacturing operations, for in burning the sulphur is separated, and, by union with oxygen of the air, forms sulphuric acid, which latter acts very destructively upon all iron plant and apparatus. Again, in gas-manufacturing, when such coal is distilled, some of the sulphur, taking hydrogen, forms dihydric sulphide, whilst other portions, by union with carbon, produce carbon disulphide.

It is said that the spontaneous combustion, which frequently takes place in coal-mines, depends upon the decomposition of this iron pyrites; for, if moisture be present, the bisulphide becomes converted into a sulphate; and during this change so much caloric will be evolved as to inflame the carbon under favourable conditions.

Varieties of coal are selected according to the requirements of the manufacture for which they are intended; and thus 'steam-coal,' 'gas-coal,' and the like have become common terms; for, in the former case — namely, the generation of steam—a strong anthracite is useful, while for gas-making a fusible coal would be preferred. Again, for the reverberatory furnace flaming coal is most valuable, provided it does not cake upon the grate, so as to diminish the draught too much. This is especially true of coal for iron-working; for, while a coal containing much carbon is best, it must yet have hydrogen and oxygen sufficient to cause good combustion without caking.

Anthracite, as already observed, contains little of the bituminous matter, and does not cake: hence, consisting principally of carbon, it forms a good iron fuel.

We may now consider a yet more primitive and natural fuel, viz. wood, which, in countries where coal is scarce, is employed not only for domestic purposes, but even in metallurgic operations. It is the hard tissue of trees, and is composed, like its derivative coal, almost entirely of organic matter, but containing, again, small quantities of inorganic. The former consists of woody matter, arranged in such a porous or cellular manner as to be traversed during the life of the plant by fluids, as sap and water. In addition to these, each species contains its own peculiar extractive matters: thus, the fir tribe contains turpentine and resin; the oak, tannin; others, gums, gum-resins, and the like: but it is the woody matter which is the combustible portion, although this property may be increased or diminished according to the nature of these peculiar principles.

The density of woods is, in all cases, greater than that of water, their apparent lower specific gravity depending upon their porous structure enclosing much air. Thus it has been curiously shown by Count Rumford that, when freed from air, all species have a remarkable identity of specific gravity, being all about 1·46 to 1·53.

Their specific gravity has a tolerably wide range, as will be seen in the table here given of some of the more common varieties:—

Ebony	1·33	Elm	·67
Heart of Oak	1·17	Willow	·58
Boxwood	·91	Male Fir	·55
Beech	·85	Poplar	·38
Ash	·84	Cork	·24

The value of woods as fuel may be estimated by taking, first, their density into account, and, secondly, the amount of water they enclose; for the greater the density the more solid carbon they contain in a given space; and, on the other hand, if they possess much water, a large amount of this carbon is expended in converting the water into vapour, which carbon is thus lost as to effective work.

For this reason fresh-cut woods are quite unfit for fuel, for they then contain water ranging in quantity from 18 to 50 per cent. Much of this is got rid of by drying, as it is hygroscopic water; but even after two or three years about 15 per cent will be retained. The drying is often effected in large chambers or kilns, heated to about 250° to 260° F., or 121° to 127° C. In metallurgic operations where wood is used this drying is essential, and there are many works in which wood is thus employed as fuel: thus, in some mercury-works, in roasting copper ores at Mansfield for separation of silver, in some of the Swedish iron-works (in the latter they dry the wood by combustion of the waste gases from the furnaces), and in many other places, not only where coal is scarce, but also where the peculiar qualities of the combustion are desired.

The great range of water above mentioned depends much upon the time of year at which the wood is cut and examined. Thus Schubler states that ash felled in January will contain 28·8 per cent of water, but if felled in April, 38·6. Light porous woods, from containing much air, give a brisk combustion, but at the same time rapidly consume the charcoal formed. For these reasons light woods are preferred in porcelain-works, glass-manufactories, and the like, where it is required to give a uniform temperature to bodies in large masses. They contrast strongly, in these respects, to dense woods, which consume slowly, and thus form a dense charcoal upon the surface, which burns slowly away. Hence, for stoves, furnaces, or steam-boilers, such are to be employed.

At the close of the combustion of woods we find an ash remaining consisting of inorganic salts. Their bases are potash, soda, lime, and magnesia, and in some cases oxide of iron. These are united with carbonic, phosphoric, silicic, and sulphuric acids, and also with chlorine.

Peat is an incipient kind of fossil fuel, consisting of decomposed vegetable matters, containing the remains of mosses and aquatic plants. It constitutes the brown soil found in bogs in Holland, Ireland, and other places.

In Holland these bogs average about six feet deep, but in Ireland they are often thirty or forty feet. Hence, in such places, it comes into use as a fuel, and in its ordinary dense state possesses about half the heating power of coal. It is used in lead-smelting by the Scotch hearth.

After what has been stated with regard to the natural fuels, wood and coal, it will perhaps be seen that for many operations the actual carbon, free from much of the associate elements, would be most desirable. In the case of wood, this is called charcoal; and when from coal, coke.

Charcoal is really our most valuable fuel for small operations, although large ones are just as advantageously carried on by it, its cost limiting its use. Thus, some two centuries since, when wood was plentiful in England, all our iron-smelting was done by charcoal; and even up to the present time it has been the fuel employed for the gold and silver melting in the Mint melting-house.

The manufacture of charcoal is said to have been carried on for 2000 years. Its principles are the heating of wood with only just such a supply of air as suffices to keep up a kind of distillatory process, care being used that it is not enough to allow of actual combustion; together with this, the carrying it on sufficiently slowly to ensure the hydrogen and oxygen of the woody fibre uniting, and not taking any of the carbon to form other products.

The most simple operation for effecting these is charring wood in a heap; it is practised both here and on the Continent. The yield of charcoal is by it equal, if not superior, to other processes; but, on the other hand, all secondary products are lost by escape into the air.

The wood is first cut up into convenient lengths, and partially dried. The charcoal-burner then, having chosen a moderately dry and well-sheltered spot of ground, commences his pile. If too dry, it would afford air to the heap; and if, on the other hand, too wet, heat would be lost in generating watery vapour from the ground, which, passing through his charcoal, would be decomposed at its expense. The pile is commenced by driving in three central stakes, round which the wood is ranged perpendicularly, to the diameter the heap is to measure. Other logs are stacked upon this first layer, then a third set, and so on, till a conical pile is formed. Down the centre a quantity of charcoal and brush-wood is put between the central stakes, or quandel, as it is called. This fuel is inflamed, and the heap then covered tolerably close with turfs, but some small openings are left on each side at the lower part for the escape of the vapour formed. The fuel is replenished as it burns away, until the heap itself is in partial combustion. The first stage is called 'the sweating,' during which the watery vapour is expelled; when this is over the charring is allowed to go on for several days, the carbonisation being regulated in a certain order, for which the utmost care is taken in regulating the draught. For this purpose chimneys are opened in the pile where required, so as to give the volatile gases evolved ready escape into the air, lest by passing over the burnt portion waste would be caused. Thus constant watching is requisite, and towards the end the heat has to be conducted towards the outer rings, in order to carbonise them, a step rendered the more necessary by the cooling effect of the outer covering, increased as it is by the constant deposit of evaporating matters upon it.

When the operation is complete, flame issues around the heap, and if any parts do not exhibit this, holes are opened to induce it. The pile is now 'choked' by carefully covering it up with a layer of humid soil. Twenty-four hours generally suffice to cool it down; if it be not, some soil is taken off and fresh damp earth covered over the spot. And when all is cool it is drawn; any which may remain incandescent being watered, or covered up to extinguish it.

On the Continent, where charcoal is largely prepared, the process is the same, but the wood is placed horizontally; a more economical way, but, on the whole, our charcoal is said to be of better quality.

Charcoal is sometimes prepared by distillation of the wood in close kilns, or iron retorts, by which acetic acid, tar, and volatile products are collected, and the charcoal left as a residuary matter. This charcoal, however, is never so good as that prepared in a heap. The specific gravity of charcoal ranges from 1·4 to 2·0, according to the kind of wood from which it has been made; also to the temperature employed. It should have a ringing sound when struck, a conchoidal fracture, and a jet-black glossy colour. Fresh charcoal soon absorbs gases and moisture, so as to increase some 10 to 20 per cent in weight. It burns with scarcely any flame, the small amount playing over its surface being due to the combustion of carbonic oxide, for the carbonic acid first formed on combustion of charcoal is deoxidized in passing up through the burning mass, and from CO_2 becomes CO, which burns with this blue flame.

Coke bears the same relation to coal that charcoal does to wood; and its formation is by similar means. As it is an object in many metallurgic operations to get a dense fuel, that is to say, one containing as much combustible matter as possible in a small space, it is necessary to prepare coke specially, otherwise it is readily to be had, but of a lighter and porous character, as a residue from gas manufacture.

In preparing coke for itself alone, the coal is carefully selected, and its method of preparation adapted to its after uses. For example, in iron works, it is necessary to have a coke which is not friable, otherwise the weight used in the furnace would crumble the underneath portions, and so cause much dust and obstruction to draught. For these operations, then, it is generally prepared on the spot, and in simple heaps.

The coal is made either into a long rectangular heap, or else into a circular mound. If the former, it is of about 180 feet long, by 10 to 12 broad, through this a hole or channel is made during the heaping of the coal. The heap so completed, a hole is made at regular intervals with a stake, passed from the top down into this channel. The heap is now ignited by putting hot coals into the holes just described, and the coking commences. The heap is watched, and regular combustion ensured by assisting or by checking the draught in those parts in which it may be required. The operation completed, the combustion is arrested by a good cover of ash, and after two or three days, in which time it will cool down, the heap is removed, and the coke quenched by water.

The same operation is sometimes performed in mounds, in which case a single perpendicular flue is made as in the charcoal mound, and then, by leaving openings here and there around it, the draught is directed, or conducted all over the heap. Both these operations are, however, rude and uneconomical, in comparison with the oven process; but, on the other hand, their being carried on upon the moist and naked ground, affords a means of purifying the coke from sulphur, for a current of watery vapour sets up through the heap, which by decomposition affords its oxygen to the sulphur, converting it into sulphurous acid, while the hydrogen, set free, takes a portion of the carbon forming carburetted hydrogen.

If, however, the sulphur exists in the coal in combination with a metal, as a sulphide, we then get the metal oxidised and dihydric sulphide acid given off. Calvert and Chenot employ sodic chloride in coking for that employed in iron works, by which they get rid of the sulphur.

In the plan of oven-coking as carried on in England, a series of five or six brick-built ovens are generally placed side by side; at times also the volatile products (which as a rule are disregarded) are collected. Thus in some works, gas-making is carried on, by some such arrangement, so that a dense and valuable coke is left after the distillation of the gas.

The ordinary dimensions of these ovens are about 10 feet in width by 12 in depth, and 8 feet high, with walls built of about 2 feet thick in fire-brick, the roof being of the same, and arched over from side to side. In the crown of the arch a round opening is left for volatile matters to escape, and in front a door of about 3 feet square is formed, and generally swung by a chain and lever. Now, in operating, the charge is partly introduced by the door, but completed from the top, by which the angles of the oven get well filled, and the presence of too much air is guarded against, which would cause waste.

In ordinary, from the coke being removed hot, ignition takes place as soon as a fresh charge is introduced; if it does not, hot wood is placed in the front door: quantities of gases are at first evolved, so that the top door is left open, and the front partially so, when these cease they are closed, and after the final completion of the operation and a slight cooling, a jet of water is thrown in by a hose.

This not only brings the temperature of the coke down so as to allow of its removal, but also by generating steam, affords elements for the final expulsion of the sulphur, as described in mound coking, while the coke left is of a denser, brighter, and more sonorous character. Care is, however, taken that the cooling down of the oven is not carried too far, for it is found that when the fire-bricks are well heated, the coke is of a better quality and less spongy, than the first charges of a newly lighted furnace would be.

An excellent kind of coke is now made from gas tar, being left as a residue in the retorts after the volatile products have been eliminated from it. Thus, Dr. Ronalds is now making this fuel (at his works at Edinburgh), which is nearly pure carbon;

he gets it as a remainder after having obtained creosote oil from the tar. A specimen of this tried by the author was found to be excellent, but it must be broken up to the most useful size to insure its full heating effects.

In considering the application of the above solid fuels for smaller metallurgic operations, it will be seen that the more useful ones are charcoal, anthracite coal, and coke. Wood may be dismissed with the observations already made upon its disadvantages, the principal ones being the large bulk of heating material required for a moderate amount of heat, and next loss of heating power in getting rid of water and volatile organic products.

But in charcoal we have a fuel not to be equalled for all delicate operations, being quite pure carbon, and, above all, free from sulphur. On the other hand, for larger operations its cost is very considerable; while for small ones, from its porous structure and its compact nature, it must either be broken into pieces of a convenient size (about that of a large walnut, for instance), or else very large, and consequently inconvenient, apparatus must be employed.

On the whole, anthracite will be found most applicable. It is of all coal the most dense, and capable, in a small fuel space, of affording a large concentrated heat. Then the amount of water it contains, being small, is not enough to cause waste of heat in vaporising it; while, on the other hand, it effects the splitting up of larger portions into effective-sized fragments. This is a point of vital importance in most furnace operations, but particularly so in muffle or cupelling furnaces, where the fuel should be uniform in size and quite free from dust.

Coke may be classed with anthracite as to its characters; both are difficult to kindle, from the absence of volatile inflammable matters; for, in the combustion of coal, the first application of heat distils off some of these, which, at once igniting, kindle the carbon; but in coke or anthracite the heat has, unassisted, to act on the carbon. Coke is better broken at once into lumps of a fit size, for, as it contains no water, it does not break up in burning like anthracite.

The denser the fuel the more concentrated will be the heat produced. For example, a given weight of charcoal may give the same actual amount of heat as a given weight of anthracite; but, as the former is light and incompact as compared to the latter, so will the heat of the former be expended over a larger surface than the heat of the latter, whose effects are more intense from being exerted in a more confined space.

Supplementary to solid fuels, both for large and small operations, may be added gaseous ones, as already stated in describing gas-heating apparatus. Their use is daily extending in all directions; for, in the use of solid fuels of any kind, there is always much loss of heat—that is to say, the amount of fuel expended is much in excess of what is really required to do the actual work needed. This, together with the power of obtaining such intense heat, and in large body, from the use of gases, led the Messrs. Siemens to apply solid fuels rather to the production of gases, the latter to be employed in the actual work itself; and notwithstanding the need of extra apparatus, the economy of fuel is immense, as all conditions for effecting this saving are perfectly fulfilled; and it is difficult to foresee to what extent their furnaces will be used, so intelligently have they worked out all points tending to their universal application.

There are two methods by which the heating power of fuels may be determined experimentally:—

The first is that of Count Rumford, and consists in finding how many pounds or ounces of water will be raised one degree Fahr. by the combustion of one pound of the fuel.

The second is the method employed by Berthier, and depends upon the power of carbon or oxygen when heated with oxide of lead to reduce the lead, the calorific power being deduced from the amount of metallic lead obtained.

The methods of Rumford, Ure, and others (similar in principle), were carried out by burning the fuel in a close vessel, and causing the heat of it to pass through a worm-like flue traversing a vessel of water, to which latter the whole of the heat is communicated; and then the consequent rise in the temperature of the water is measured by a properly arranged thermometer; but care must be taken that the radiation from the surface of the metallic vessel is calculated for, or else provided against; also it should be secured, that the escaping air from the worm or flue should be of the surrounding temperature — that is to say, that it should have given up all its derived heat to the water.

Rumford's apparatus was a copper vessel, 4¾ inches deep by 8 inches long and 4½ broad. Through this a copper worm was coiled three times round and passed out at the top. Where it entered below it was expanded out into a large funnel, under which the fuel to be tested was burned, care being exercised that it was done in such a manner as that all the heat traversed the coil.

Kerl gives the following table of the heating power of the substances named, so determined:—

1 of Hydrogen	will heat 1° C.	23600	of water	3·03
1 of Carbon	„	7800	„	1·00
1 of Charcoal	„	7500	„	0·96
1 of Good Mineral Coal	„	6000	„	0·77
1 of Dry Wood	„	3600	„	0·46
1 of Turf	„	2500 to 3000	„	0·33 to 0·38

'These ratios, or units, represent, therefore, the relative quantities of heat which are required to raise the temperature of one part by weight of water, usually one pound, one degree centigrade. The figures are simplified by taking carbon as the unit, and dividing them by 7800, when the second column above will result.'*

For Berthier's plan, he powders 5 grains of the fuel, and intimately mixes it with about 150 to 200 grains of litharge. The mixture is packed closely in a clay crucible, and covered well with a layer of fresh litharge. The crucible is then well luted up, placed in the fire, and heated, until the whole of the carbon and hydrogen is burned.

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* Crooke's Translation of Kerl's *Metallurgy*, vol. iii. p. 320.

The mass swells considerably from the escape of water and gases; but, towards the end of the operation, the crucible is gradually raised to a full red heat, after which the metallic particles, reduced from the litharge, are agglomerated by a few gentle taps of the crucible on a stone. When cold, the pot is broken, the button of lead detached from it cleaned from inorganic ash and slag, and weighed. From the number thus arrived at, the amount of oxygen required for the combustion is calculated. Thus, where pure carbon has been tested, it is found that 34½ times the weight of metallic lead has been reduced. This, then, affords a point of comparison. Some figure must next be assumed to represent the heating power of pure carbon, and Mr. Andrews (an experimenter upon this subject) has taken the number 7900. Thus we have data for further calculation.

Suppose, then, in examining a specimen, we found that 25 grains of lead were reduced; we then say, as 34·5 (the weight reduced by pure carbon) is to 7900 (its assumed heating power), so is 25 (the number of grains now reduced) to the heating power of the specimen, which would give the number 5725 (nearly) as the result sought.

For 34·5 : 25 :: 7900 : 5724·6.

But it may be anticipated that coal, wood, &c., from containing other elements, would possess heating power by virtue of the hydrogen, or hydrogen compounds, so contained. This is true, and the process is not accurate where the fuels contain carbon and hydrogen in varying proportions. Percy, speaking of Berthier's process, says, 'Three parts by weight of carbon reduce the same quantity of oxide of lead as one part by weight of hydrogen. But the calorific power of carbon and hydrogen respectively are, in round numbers, as 8 to 34. Hence the same weight of lead obtained by reduction would, in the case of carbon, indicate calorific power of 24; and in that of hydrogen 34. So that the process is inapplicable to the determination of calorific power of fuel containing variable proportions of carbon and hydrogen.'

It is often necessary to ascertain the temperatures at which many operations which are carried on at higher ones are effected, although more upon scientific considerations than practical ones, because, for the latter, the eye is commonly a sufficient guide. For instance, all persons engaged in metallurgic operations at once understand what is meant when we speak of a dull red, a full red, or a white heat. It is for bringing these terms into a numerical shape that the instruments called 'pyrometers' are used. C. W. Siemens, speaking of these terms, designates them as expressions which remind one rather of the days of alchemy than of chemical science of the present day.

Pouillet gives the degrees by such means of several well-known heat colours. Thus, a dull red can be estimated at 1292° F. = 700° C.; cherry-red at 1652° F. = 900° C.; orange-red at 2192° F. = 1200° C.; and a bright white heat at 2552° F. = 1400° C.

A good and trustworthy pyrometer has up to very lately been wanting, but the one lately devised by Siemens appears to be perfect for all ranges of temperature from a very few degrees of elevation, up to the highest furnace heats. It is founded upon the electrical resistance offered by conductors when heated up, and was described by him at one of the Friday evening meetings of the Royal Institution, and published subsequently in their Proceedings.*

The pyrometer of Mr. Daniell has been the one hitherto employed in all cases where high temperatures had to be measured; in it the expansion of a bar of platinum is made the means of estimating. Wedgwood's depends on the contraction of a piece of clay. Prinsep's pyrometer is founded on the melting points of difficultly fusible alloys; and Captain Brystrom's upon the heating up of a certain quantity of water by a ball of platinum previously heated in the hot temperature to be determined.

In Prinsep's pyrometer the fusion of alloys of gold and platinum is employed as the measure. He takes the fusing point of gold, which Mr. Daniell has fixed as 2016° F. = 1102° C. as his zero, and that of platinum as his highest point to be determined. Then, beginning with pure gold, he adds 1 part of platinum successively for an increase of every 1 degree (arbitrary) of temperature. Suppose, then, a series of beads of metal are made; the first of 100 gold, then 95 gold + 5 platinum, 90 gold + 10 platinum, 85 gold + 15 platinum, and so on, up to pure platinum; such a series would indicate increase by steps of five degrees.

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* *Proceedings of Royal Institution of Great Britain*, vi. 438.

A fit series of these are placed in a small refractory vessel, with a close fitting lid. The arrangement is exposed to the temperature to be ascertained, and indicates the height of the degree by the alloy of least fusibility which it is capable of melting.

In the pyrometer of Mr. Daniell, the result is arrived at by ascertaining the expansion that a small bar of platinum undergoes by exposure to heat.

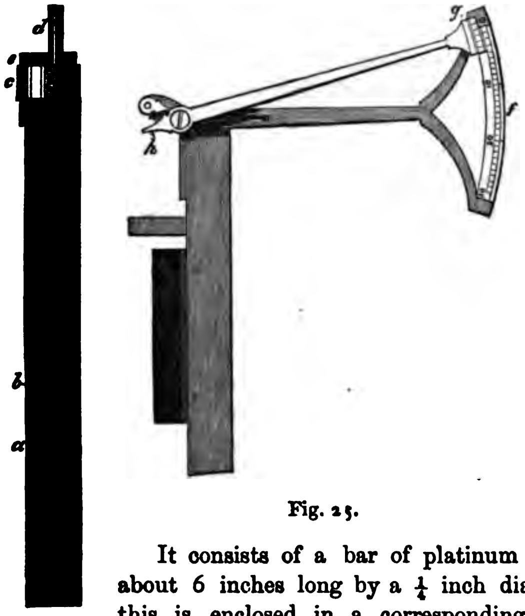


Fig. 25.

It consists of a bar of platinum (*a*) of about 6 inches long by a ¼ inch diameter; this is enclosed in a corresponding cavity bored out in a bar of well-baked black-lead crucible ware (*b*), which is formed with a shoulder rising above the cavity on one side. Against this a short index-piece of porcelain is laid, passing down the cavity and touching the outer end of the platinum bar when in its place. This index is then strapped by a platinum ring and a porcelain wedge to the shoulder of the black-lead bar. As the expansions are small in so short a piece of metal, and, moreover, are actually differences of expansion between the platinum and the black-lead ware, a scale is used to measure them, where a radius arm (*g*) is so disposed on a graduated arc (*f*) as to multiply the indication. In using this pyrometer the platinum bar and index having been firmly strapped in their places, the radius-arm is adjusted to zero by bringing the knife edge (*h*) just into a notch formed for it on the top of the index-piece. The platinum bar and case is then exposed to the heat to be measured. By this the metal will be elongated, and as it is confined by the bottom of the cavity of the black-lead bar, the expansion will take effect at the top end, and it will push forward the porcelain index. Then as it cools, although the metal bar will retract, the index remains at the point to which it was forced out, having been kept there by the platinum strap. It then only remains to measure the amount of extension as shown by depression of the index upon the graduated arc mentioned.

Now although the degrees are arbitrary ones, they are got by comparing each instrument by experiment with a good mercurial thermometer, and so in their value they follow on those of the Fahrenheit scale.

Siemens, in describing his instrument, speaks first of the air-thermometer of Galileo, and states that the expansion of a permanent gas at a constant pressure is the most perfect index of temperature; and that his instrument 'presents many points of analogy if we substitute electrical "resistance in conductors" for "expansion of gases." Both these effects are functions of temperature increasing with the temperature according to progressive laws, which, in the case of the gases, we call the *law* of *Charles*, and in the case of conductors, the law of *increase of electrical resistance* with temperature.'

In Siemens's pyrometer he sends a battery current through 'two branches of equal resistance, each branch comprising a free spiral wire of platinum, and one of the coils of a differential galvanometer;' then by heating one of the spirals in the temperature to be measured, the needle will be deflected by the current resistance in this wire, and its deflection may be made the measure of the temperature. In the arrangement for measuring high temperatures a platinum conducting wire is coiled on a cylinder of baked porcelain, and in a helical groove to prevent contact in the coils; this groove is deep enough to protect the coil also from contact with the outer platinum case in which the whole is enclosed for insertion into the furnace or temperature to be measured. Three leading wires of insulated copper, united in a light cable, connect the pyrometer with the measuring instrument, which may be at a distance of some hundred yards from the same. They are connected by means of binding screws at the end of the tube to three thick platinum wires, passing down the tube to the spiral of thin platinum wire. Here two of the leading wires are united, whereas the third traverses the spiral, and joins itself likewise to one of the two former, which forms the return wire for two electrical circuits, the one comprising the spiral of thin wire, and the other returning immediately in front of the same, but traversing in its stead a comparison coil of constant resistance.

The indications are not, however, given by a differential galvanometer, as it was found that the use of so delicate an instrument is 'attended with considerable practical difficulty in iron works, and other rough places where it is important to measure elevated temperatures.' Hence for such he employs a differential voltameter, consisting of two tubes fixed on a scale showing arbitrary but equal divisions. These are arranged so as to be capable of being filled from little reservoirs with acidulated water, up to the zero marks of the scale. Each has two small platinum electrodes. Here the indication is given by the difference of level in the liquid in the tubes caused by the unequal rate of decomposition by the two currents, viz., the constant resistance one and the other from the heated conducting wire.

Some working results of the pyrometer were shown, and by the same protected coil, a mixture of ice and water, boiling water, molten lead, and the fire in which the latter was melted were tested; and the readings given were 2° C., 98° C., 330° C., and 860° C., respectively. And Mr. Siemens stated that Professor Bolzani, of Kasan, has used it for recording the temperature at elevated points, and at points below the earth's surface. And Mr. Lowthian Bell has employed it in his blast-furnace researches; and at several iron-works 'pyrometer tubes are introduced into the heating stoves, and permanently connected with the office, where the heat of each stove can at all times be read off and recorded.'

The reader is referred to the lecture quoted as above for full description and diagrams of the apparatus.

As Mr. Wedgwood's pyrometer is even now frequently referred to in scientific works, it must be briefly described, although but for the purpose of showing that its indications cannot be depended upon. It is founded upon the principle of the contraction occurring in a piece of fine clay, by exposing it to the temperature desired to be measured. This contraction occurs from the clay (a compound of alumina and water) parting with its water by heat. But it has been proved that long exposure to a comparatively low temperature will effect this just as well as the quick action of a high one, added to which, for each operation a fresh piece of clay had to be employed, and perhaps no two specimens were uniform in composition. Hence the instrument is useless, although simple in its construction and manipulation. It consists of two brass rules, fixed upon a plate, and gradually converging. This guage, as it may be called, is divided into 240°, each one of which Mr. Wedgwood supposed to be equal to 130° of Fahrenheit's thermometer scale. Then, for use, a cylinder of clay was passed up the guage, and the point noted; the clay was next exposed to the temperature to be measured, when the difference between the scale degree to which it now passed up and the former one was presumed to be the temperature sought.

CHAPTER VI.

NOBLE METALS.

Mercury.

Mercury has been known from the remotest times, a fact not surprising when we observe the thoroughly metallic appearance of the native metal, a state in which much of it frequently occurs. But the first really practical notice of mercury is by Dioscorides, who describes a method of reducing it from cinnabar, or, as that ore was then called, minium; a misnomer, said by Thompson to result from its being adulterated with red lead. As an apology for this admixture it may be stated that the natural colour of the cinnabar was modified by the red lead, for the ancients used cinnabar very largely, not only in the arts of decoration and painting, but also in the less civilised countries to paint their bodies; and this with impunity as regards any mercurial effects, as it is one of the inert mercurial compounds. And in articles which have come down to us the permanence of the colour after the lapse of ages is somewhat remarkable.

No doubt the first supplies of the metal were from native mercury; and thus Pliny distinguishes between such metal and that obtained by reducing the ores; designating the native metal as Argentum Vivum, the reduced as Hydrargyrum, whence it is doubtful if he believed them to be the same metal. He also distinguishes between cinnabar and minium. At the present time the chief supplies consist of reduced metal from the ore; and are derived from California, Spain, Austria, Mexico, Peru, and also from China and Japan. Small quantities are also found in the

Palatinate, left bank of the Rhine, France, and Tuscany. The ores are the following:—

First, Cinnabar or mercuric sulphide; this is an ore of a brown-red colour streaked with scarlet, the latter colour being due to nearly pure vermilion. The latter, according to Sefstrom's analysis, is composed of 86·29 parts of mercury, combined with 13·71 of sulphur; but the native ore gives very varying proportions of these two components, depending upon the locality where it is found. Thus, 100 parts of ore from the mines of Almaden in Spain are composed of mercury 36 to 41 parts, sulphur 16 parts, and foreign matters, such as gangue, other metals, silica, water, &c., 43 to 48 parts. The ore from Idria in Austria contains mercury 51, sulphur 8, and foreign matters 41. Californian ore, mercury 70, sulphur 11, foreign matters 19. While that from Japan is nearly pure cinnabar, being composed of mercury 84, sulphur 14, and foreign matters only 2. Of foreign associations re cupellous sulphide, ferric oxide, and alumina are the chief.

Second, Horn quicksilver, or native calomel, so called from its translucent, yellow, horn-like appearance; it has also a horny cut, but is sometimes found crystalline. It is a chloride, and chiefly found at Idria. Iodides and bromide also are found, but more rarely.

Third, Native Amalgam. This is sometimes formed by silver and mercury alone; at other times gold is associated with these.

Fourthly, much mercury is found native, and in some of the mines it trickles out from crevices in the ore, and collects in any adjacent hollow. It occurs in globules disseminated in primitive rocks, which latter have the appearance of hardened clay. Mercury so collected is nearly, if not quite, pure, but sometimes it contains traces of gold and silver. The great mine at Idria is situated in the body of a mountain; and it is generally reported to have been discovered nearly three centuries back by the trickling out of the native mercury from a fissure through which a small spring discharged itself.

The mines of Idria are in the possession of the Austrian Government, and produce about 150 tons of the metal annually.

This is said to be about a fourth of the quantity which might be obtained from them, the working being checked as to quantity, in order to keep up the price of the mercury. But they have also vermilion works here, at which, in addition, about 90 tons of vermilion are made during the same period.

It is found that lime will very readily separate the sulphur from mercurial ores, hence in the best-worked establishments this body is employed, by being mixed with the ore before the after-furnace operations. But a second and more primitive method of reduction is carried on at both the Idrian and Almaden works, viz. the heating of the ore alone; sufficient air being at the same time allowed to enter the furnace to convert the sulphur into sulphurous acid, and so set the mercury free.

The construction of the furnaces for effecting the reduction at the Idrian works may be explained by the accompanying diagram.

A fire-chamber, *a*, is placed at the lower part of the body of the furnace, above this fireplace are built three perforated arches, *b b b*; upon these the ore is placed, the poorer kinds, being broken into somewhat large portions, are placed upon the lower arch, so as to fill the space between it and the second. Next, on the second arch are heaped the smaller fragments in the same way; while upon the third is arranged a series of trays or pots containing ore dust, mixed with some residues of former workings. Adjoining this furnace on each side are large air-chambers, *c c*, for the supply of oxygen to the sulphur of the ore. From the upper or tray compartment a flue passes out on each side into a large condensing chamber, *d*, entering near its top. Of these chambers there are six on either side of the furnace, constituting two distinct sets; the chambers in each set communicating by openings alternately at top and bottom. From

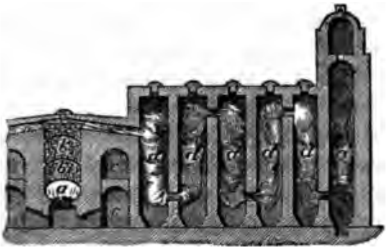


Fig. 26.

the sides of the last one, a series of flanges projects in a slanting direction, almost from side to side, and upon these a stream of water is kept flowing from the top to the bottom. This last is also higher than the others, and terminates in a chimney for the escape of any sulphurous acid or uncondensed vapours which may pass through the entire set of chambers. The whole of this apparatus is doubled, by a second series being built at the back of the first. The dimensions of the face of the arrangement are 180 feet long by 30 feet high.

In working, the furnaces are first charged with ore, and the openings and doors luted up (there being an opening into the top of each condensing chamber); next, a good brisk beechwood fire is kindled in the grate, which is sustained until the furnace and ore are of a cherry-red heat, which takes place in from 12 to 15 hours. Distillation will then commence, and as long as this goes on the heat is carefully kept up, the space of time being generally about 12 hours. The mercurial vapour becomes highly heated, and thus causes a strong draught through the condensing chambers, and consequently from the air-spaces into the body of ore operated upon. The vapour passes into the first chamber in company with the sulphurous acid resulting from the oxidation of the sulphur, some sublimed vermilion, and a quantity of soot, the latter two being deposited upon the walls. The mercury condenses in drops upon the stone floor of the chambers, which being inclined to one side, where there is an exit-pipe, it flows thence to a reservoir.

As the operation proceeds the temperature of the apparatus rises, and condensation of the metal takes place in consequence farther from the furnace, even to the last chamber; but here it is assisted by the cold stream of water, as also by extra height in this terminal one.

When distillation is over, all is allowed to remain closed for about five days, so as to cool down. The upper openings are then unluted. Thus a current of air rushes in which assists in cooling down the arrangement. The soot and vermilion are then removed from the walls. These are put aside to be reworked, for which they are placed in the upper trays of the furnace at a future working.

The walls are well brushed down, and the whole produce of mercury filtered through linen, when it is packed in the iron bottles (containing about 70 lbs. each) in which we obtain it. The walls, however, absorb much mercury.

It will thus be seen that a week is occupied in each working, and as soon as the apparatus is cleared a fresh charge is introduced. The charges average about 56 tons, and, by the employment of about forty workmen, this is got into the furnace in three hours. The produce of mercury amounts to about 4 to 4½ tons.

It is said that at Idria the operatives are in a most sickly and enervated state, and that the cleansing of the condensing chambers in particular is a most unwholesome operation.

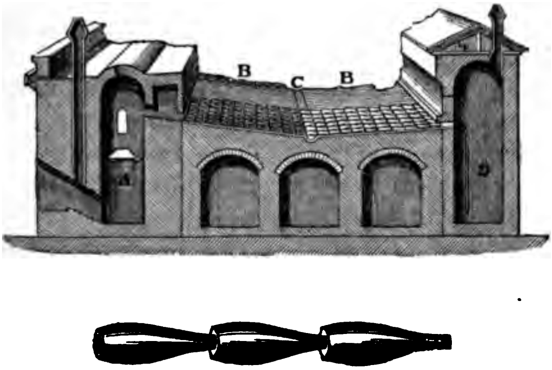
The absorption of metal by the porous walls, and other evils of the old plan, led to the adoption of wood condensing tubes surrounded by water to cool them. Cast-iron was also employed, but the practical inconvenience of their been attacked by the sulphurous acid formed led to the substitution of wood.

Alberti devised a plan at Idria for poor ores, viz., such as contained only about 1 per cent of mercury, using a reverberatory furnace. About 3 tons are operated on at once, three-fourths of which is spread over the bed and heated to redness by a wood fire. The doors are luted up during heating, and opened occasionally to turn the ore. As working progresses it is brought forward in separate portions to the hotter part of the furnace, and the remaining fourth of the ore thrown in at the back towards the close of the operation. Condensation is effected as follows:—From a small brick condensing-chamber directly at the back of the reverberatory a long wide iron tube passes backwards sloping slightly downwards at the same time. It ends in a larger arched brick condensing-chamber, which latter opens into an upper one built above it. From this again a second tube is carried forward again, and ends in the base of the flue above the reverberatory. Above these iron tubes are water trays from which a constant dropping of water is carried on upon the tubes so as to cool them and condense the vapours within.

The plan of working is, as already stated, to draw the ore forward into the hotter and front part of the bed in alternate quantities, giving it at last such an amount of heat as shall be sufficient to drive all the metal from the poor ore. The greater part of it is found to condense in the lower iron tube. Full 95 per cent of the whole being collected there. There is always also a residue of soot, vermilion, and finely divided mercury passed over, which is separated for reworking.

At the Spanish mines of Almaden the same principle of work is carried out, viz. the reduction of the ore by air alone; but, as regards the manipulation, it is, if anything, more wasteful of labour, health, and fuel, than the old Idrian plan.

The heating is performed in a Butyrone furnace, as it is called. This is a large square chamber, A, of about 4 feet in diameter, divided into upper and lower compartments by a brick arch placed about half way up, and perforated; over this the charge is introduced, partly by a door at the back and partly by an opening at the top. And although it is placed altogether in the same chamber, yet, as regards the class and quality of ore, the same disposition is made



Figs. 27, 28.

as at the Idrian furnaces, and the fire is made also by brushwood placed in a lower chamber.

But it is in the method by which the metal is condensed that the unskilled and primitive nature of the apparatus is shown; for this is effected in a series of earthenware condensers called 'aludels' (fig. 28), which are arranged in rows or chains across a long brick terrace, B B, built up level with a series of openings left at the top of the ore chamber. This terrace, called the aludel bath, is formed by two inclined planes, erected on arches; one of which planes descends to the centre of the arrangement, at which point a transverse gutter, C, is formed. The second rises again at the same angle, to reach a large condensing chamber, D, which is built at the other end of this apparatus, and is simply a large brick chamber, having a cistern of water at its bottom. The total width of the whole system being about 65 feet.

The aludels are arranged in a kind of chain, by the point of one entering the neck of the following one. Their shape and arrangement are shown by the three figured below the drawing of the furnace. Thus about fifty will complete the chain from one end of the aludel bath to the other; of these chains there are six on each side of the bath (back and front), consequently from 500 to 600 in the series, all the joints of which, being well luted with clay, will necessarily render this luting operation one of considerable time. The middle aludels of the chains, being at the lowest level, are provided with holes at their undersides, by which the condensed metal may run both from the descending and ascending halves of the arrangement into the central gutter of the bath, whence it flows down a pipe into a receiver below, and as they are exposed to the free air, the great bulk of the metal is condensed in them; thus the chamber in which they terminate serves to condense remaining portions of vapour, which are delivered under a screen, so as to conduct them down to the condensing water at the bottom.

The charge of ore worked in this furnace at one time is about 10 to 14 tons; and upon this, firing is kept up for 12 days, when it is allowed to go out; the system being then cooled, the aludels are separated, carried one by one to the centre channel, where they are emptied; any metal spilled also flowing to this, from the inclination of the bath. The whole product, together with that from the condensing tower, is then purified from soot, dirt, &c., by a very simple mechanical process, viz. by pouring it upon the floor of the working-room, at its upper end, which, being slightly inclined to the lower, allows the metal to run slowly down to the receiver placed there, during which passage the impurities are left upon the floor.

They endeavour so to mix rich and poor ores that the produce of each working shall be about a ton and a quarter; for, if too rich, the condensing arrangement is so imperfect that there will be much loss of mercury, and that to the injury of the health of the operatives.

An improvement on the Idrian condensing arrangement was made by Hähner at New Almaden, California. A series of six condensing chambers is employed, and their interior is coated with a kind of stucco, that is, mortar containing fine sand, which will give a hard, non-absorbing surface. They communicate at the bottom, and at the top of each is an iron plate kept cool by water. The chimney is also cooled by water terraces at each of three tiers in which it is built.

The furnace itself resembles very much the ordinary Almaden cupola, but is provided with a hopper at the top through which the charge is introduced. In working, the fire-bars are stopped to a certain extent by a layer of bricks and wood laid upon them; and as the first object is to get the heat up slowly, in order to diminish a rush of steam from the wood fuel, this choking of the air space has its use, although it also acts in preventing the falling through of the ore which is next charged in upon the top of some brushwood and coal. The poorer ore first, then a layer of coal, and then richer ore, and so in alternate layers. At the end of the second day working commences, and after this relays of ore, of about 7 cwt. each, mixed with three or four per cent of charcoal, are thrown in every three-quarters of an hour by the hopper. At the end of 22 hours these first charges are worked off.

But the more skilful working of the ore, effected by mixing some body with it for the separation of the sulphur, renders the work practicable in close apparatus; and the inlet of air and outlet of sulphurous acid being dispensed thus with, the mercury is capable of being at once distilled off. The bodies in use for this operation are either iron scales or lime. At the Bohemian works at Horowitz the former is used, it is mixed with the ore and placed in iron dishes; these being set, one over the other, in a vessel containing water, are then covered with an iron receiver. This is surrounded with fuel, and thus heated, when the mercury distils, *per descensum*, and condenses in the water below. A somewhat similar apparatus will hereafter be figured, as used for separating the mercury from its amalgam with silver.

At the duchy of Deux Points lime is employed, being mixed Ponts with the ore to the extent of one-fourth its weight. This mixture is heated in ordinary earthen or cast-iron pear-shaped retorts, and the product condensed in receivers half filled with water. This, however, is not clean mercury, but a mixture of mercury and undecomposed sulphide, and requires drying and redistilling with lime for its purification.

At Lansberg, in Bavaria, where the process of distillation with lime is adopted, application was made to the late Dr. Ure, in 1846, for a plan of apparatus, and in the following year the one to be described was erected, which is in all particulars very practical and satisfactory.

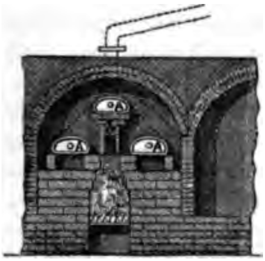


Fig. 29.

A series of three brick-arched furnaces is built, in each of which are set three large iron retorts, A, of the form used in England for gas-making. They are sufficiently large to contain a charge of, at least, 5 cwt. or more. The fire-chamber is placed directly below them, and for each three is central; but the retorts are protected from the direct action of the flames by being bedded on fire-lumps, *b*. Each three have their own flue, and all run into one central chimney. At the back of each retort (see fig. 30) a large iron pipe, C, passes down into a kind of hydraulic main, D (a large iron condenser of 18 inches diameter by 20 feet long), the pipe terminating just below the surface of the water with which the condenser is half filled. The latter is placed at a slight inclination in a trough of cold water, E, and furnished with a water-valve, by which air can enter in case of a vacuum being formed in one of the retorts, which would lead to the rushing up of the water into it, and produce an explosion. Below the lower end of the condenser is a large locked-up iron cistern, into which the mercury flows, and, being furnished with a gauge, indication is thus afforded when to open it and take out the product.

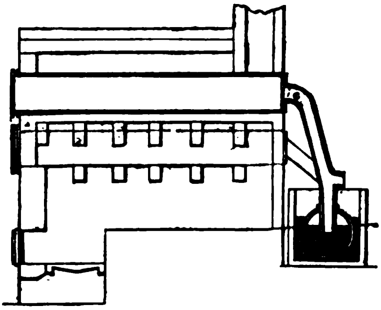


Fig. 30.

For the operation the coarsely powdered ore is mixed with quicklime, and each retort is charged with about 6 cwt. of the mixture. The heat is maintained at a uniform and requisite temperature, and thus injury to the apparatus from sudden changes is avoided. The heat being thus at once available, a charge is worked off in about 3 hours; so that from 12 cwt. to a ton of mercury could be obtained daily; and although the apparatus is efficient for any ore, it is particularly so for the richer ones. At some Californian works very similar iron retorts are used, but working into cone-shaped vertical receivers, kept cool by the evaporation of water constantly dropping on them; there the ore is rich, containing about 40 per cent mercury, and it is mixed with 1½ parts of powdered quicklime. The heat employed is a fair red heat.

Such are the methods of obtaining commercial mercury, and although frequently it is very pure, yet, where zinc or bismuth has been associated with the ores, these metals are sure to have distilled over with the mercury, and contaminated it.

Again, in commerce, it is often fraudulently adulterated with lead, tin, or bismuth, which are readily soluble in it; hence, as it is, for scientific operations especially, required quite free from such admixture, methods of purifying it must here be considered. As tests of its purity, it may be dissolved in nitric acid, when if pure, after evaporating to dryness, all should volatilise. Again, it is known to be impure if on shaking it in a bottle with air any black powder is formed, or if when poured out on a clean surface, and then gently inclining the same, the globule rolls in an elongated form, and leaves a dirty streak upon the surface.

Although distillation of the metal is commonly recommended as a means of purification, it is an uncertain one, for, as before remarked, zinc and bismuth are sure to distil over with it, if one or other be present; or if not very carefully done, the metal itself is apt to spurt up, and pass over into the receiver. If, however, this method be employed, a strong glass retort should be used, and filled about one-third with mercury; next, upon its surface, is put a layer of clean iron filings, or turnings, amounting to a quarter the weight of the mercury. The retort is then bedded in a deep sand-bath, and a good inclination given to its neck; this is lengthened by a cone of paper, which is made to dip just below the surface of the water, with which the receiver should be half filled, the receiver itself being kept thoroughly cool by placing it in a basin of cold water. The quantity thus operated upon in glass should never exceed 2 or 3 lbs. weight. If it is required to purify a larger quantity at once, an iron retort must be employed, which may be well formed by one of the bottles in which mercury is packed for transmission. To such a bottle a piece of iron gas tube may be screwed in to connect it with the receiver.

Upon the surface of the distilled mercury, at the conclusion of the operation, there is very commonly a film of oxide, and it may even chance of ferric oxide also; a small quantity of hydrochloric acid put upon this will generally dissolve it, after which the mercury must be washed with water, and dried at a gentle heat. It is therefore better to cover the mercury in the retort with $\frac{1}{10}$th its weight of coarsely-powdered cinnabar, in place of iron turnings. The sulphur thus afforded converts foreign metals into sulphides, mercury being set free at the same time.

All things considered, it is better, in place of employing mercury at all, to operate upon a pure mercurial compound, which is decomposable by heat. And there are three which may be so treated; the sublimed sulphide, or vermilion, the chloride, and the red oxide. The first two must be treated with one part of lime; but if the third be used, simple distillation suffices. But here the product is apt to have a film of oxide reproduced under the influence of the heat, although, if it occur, it may be removed by a little warm nitric acid, made very dilute.

There are, however, methods of purifying mercury without distilling, namely, by digesting it in agents capable of dissolving out, and combining with impurities; and for such either sulphuric or nitric acids, or even mercurous nitrate, may be employed with excellent effect. If nitric acid be chosen, it should be diluted with about 8 parts of water; the mercury, put into a flat-bottomed flask, or glass dish, in a shallow layer, is then covered with the acid, and the whole digested for some hours at a temperature of about 130° F. = 54°·5 C. During the digesting, it must be frequently shaken or stirred, so as to expose it well to the action of the acid. But little, if any, of the mercury is dissolved, if it be impure. Lastly, the acid containing the foreign metals in solution is poured off, and the purified mercury washed and dried.

The manipulation is the same where mercurous nitrate is used, and for the purpose $\frac{1}{80}$th part of the salt may be employed, dissolved in a small quantity of water; but here Gmelin advises boiling for some hours. The metals removed by the decomposition of the salt will be replaced by its mercury.

If sulphuric acid is employed, it is to be often shaken for some hours with the mercury, and its strength increased in the proportion in which we may presume impurities to be present. The operation is here stopped when the acid ceases to become turbid, and the metal then washed and dried as in other cases.

Dr. Miller recommends an old but very simple means of purifying mercury, devised by Priestly, namely, putting it into a bottle to the amount of about one-fourth of its capacity, a little finely powdered loaf-sugar being next added, and the bottle stoppered; the mixture is vigorously shaken for a few minutes; the bottle is then opened and fresh air blown in by a pair of bellows, after which it is again shaken; this treatment is repeated three or four times, and the mercury then filtered by pouring into a cone of smooth writing paper, having its apex pierced with a fine pin; the sugar is left behind with oxides of foreign metals, and also a certain quantity of the mercury in a state of fine division, is retained by the filter.

Mercury may also be filtered by squeezing it through a piece of chamois leather. If previously wet, it should be dried by placing it on bibulous paper, and afterwards gently warming it.

Properties.—Mercury is always fluid down to 38° below zero, F. = 38°·8 C., at which point it solidifies, after which it may be hammered out as an ordinary metal, or even welded. It contracts considerably, and becomes crystalline in texture during solidification, exhibiting octohedral crystals.

The fluid metal is very lustrous; it boils at about 660° F. = 349°·5 C. (the point not having been very accurately determined), but it is so volatile that its vapour is given off at very much lower temperatures, even the ordinary ones of the air. Thus, if some mercury be placed in a dish and covered with a small bell jar, and a slip of gold leaf be then hung in the latter, it will, in about six or eight weeks, become thoroughly amalgamated upon its surface with mercury. Burnett (in the *Phil. Trans.* of the year 1823) gives a curious instance of its volatility. Some mercury in the cargo of a ship was packed in leathern bags. These becoming rotten, the metal escaped into the bilge of the ship. A very elastic fluid was soon evolved, which covered every metallic article in the ship with a coat of mercury, and at the same time the crew were perfectly salivated.

The specific gravity of mercury is 13·59 at ordinary temperatures, while that of its vapour, evolved by boiling, is 6·976.

Mohr states that 100 lbs. of mercury will volatilize into about 460 feet of vapour.

Mercury is readily dissolved by strong nitric acid, and mercuric nitrate formed with evolution of nitric oxide; if the acid be dilute the action is slow, and then a quantity of crystals will be deposited in the solution, these being crystals of mercurous nitrate.

Sulphuric acid dissolves it only by the assistance of heat, when a sulphate is formed, and at the same time a portion of the acid is decomposed and sulphurous acid evolved. Hydrochloric acid has no action upon it. It may be combined directly, and at ordinary temperatures, with chlorine, iodine, bromine, or sulphur. It combines readily with gold, silver, tin, lead, bismuth, cadmium, and zinc, with somewhat more difficulty with copper and iron. While for most other metals it has very slight affinity. Thus amalgams are formed which become dissolved in an excess of mercury; under ordinary circumstances these are simple mixtures. The atomic weight of mercury is 200, at which estimate its two oxides must be considered as a suboxide and a protoxide. Its symbol is Hg, from the word Hydrargyrum.

Compounds with Oxygen.—If we shake mercury with air, or oxygen gas, or with ether or turpentine, or rub it well with grease or sugar, we destroy its lustrous, metallic appearance, and get a grey powder from it; this is not, as was formerly supposed, an oxide of mercury, but chiefly mercury in a state of fine division, mixed with a very small quantity of oxide. In some of the compounds employed in medicine, supposed to contain mercurous oxide, as mercurial ointment, or blue pill; if the microscope be used they will be seen to be mainly composed of very minute globules of the metal, separated by the foreign matter employed. Their size averages about the $\frac{1}{150}$th of a line in diameter.

A true suboxide, or mercurous oxide, may be formed by adding caustic potass in excess to a solution of a subsalt,—mercurous nitrate, for example,—when it falls as a blackish brown powder. Or, some calomel may be diffused in water, potash, or soda added, and the mixture well shaken together; the black precipitate formed is then to be well washed from adherent alkali. This oxide cannot, however, be preserved in an isolated state, as simple exposure to light suffices to convert it into the red oxide, the excess of metal being at the same time set free. It is insoluble in water, and by heating is entirely decomposed, the metal being left. Composition, $Hg_2 O$. Atomic weight, 416.

The second oxide, the protoxide, or mercuric oxide, is a stable compound. It was formerly prepared by heating mercury in a mattrass, to which a very long neck was attached, in order to hinder evaporation of the mercury,—a heat just above its boiling point being used. This latter was left open, so as to allow of free access of air to the interior of the flask. At the end of a month (or thereabouts) all the metal was found to be converted into a red scaly powder,—this oxide, but this process was attended with great loss of mercury. Hence the best method of obtaining it is by dissolving either the mercuric nitrate or chloride in water, and then adding a solution of potash; a dense, bright yellow powder of mercuric oxide is then thrown down, which requires to be well washed and dried. It may also be produced by heating the nitrate to dull redness, until it ceases to evolve fumes; in this way we get a scaly red powder, but, although the same as the precipitated in composition, does not so readily enter into combination.

Mercuric oxide, or protoxide of mercury, or any of its salts, are violent acrid poisons. The protoxide is very slightly soluble in water, one part being soluble in 7000. The solution has a disagreeable metallic taste, and, on exposing it to the air, it becomes covered with a film of metallic mercury. When the yellow oxide is heated, it changes, first, to vermilion red, and at last to bluish black, but recovers its original colour on cooling. Composition, $Hg O$. Atomic weight, 216.

Compounds with Chlorine.—These are two in number, and analogous to the oxides; the first, or subchloride, known in medicine as calomel, and the second, or mercuric chloride, as corrosive sublimate.

The subchloride, or mercurous chloride, may be obtained by precipitating a solution of mercurous nitrate, by means of hydrochloric acid or an alkaline chloride. Thus a whitish flocculent powder falls, which must be thoroughly washed with boiling distilled water, and dried. But the following process is more usually employed. A sulphate of the red oxide is first made; by heating 2 lbs. of mercury with 3 of sulphuric acid, and evaporating to dryness. A similar quantity of mercury to that first taken is then added, so as to form a sulphate of the black oxide. To this a pound and a half of common salt is added, and the whole sublimed. This latter affords chlorine to the mercury to convert it into subchloride of mercury; while the sulphuric acid of the mercurial salt combines with the sodium to form sodic sulphate.

The operation may be explained by the following formulæ; in the first stage

$$Hg + 2\,H_2SO_4 + Hg\,SO_4 + SO_2 + 2\,H_2O.$$

On adding the mercury, $Hg''\,SO_4 + Hg = Hg'_2\,SO_4$.

Next in the subliming operation

$$Hg'_2\,SO_4 + 2\,Na\,Cl = Na_2\,SO_4 + 2\,Hg'\,Cl.$$

Calomel may also be obtained by rubbing 100 parts of mercuric chloride (corrosive sublimate), with 75 parts of metallic mercury; these quantities being very closely in the ratio of one proportional of each. The rubbing is continued until all metallic globules disappear; and, in order to facilitate this, as also to prevent the rubbing away of chloride as fine dust, a little water may be added, so as to moisten the whole. Finally, the mixture is sublimed as before.

The sublimed product requires to be powdered and well washed with hot water; or it may be sublimed into a vessel filled with steam, by which it will be minutely divided, so as to render powdering unnecessary.

It is an insoluble compound, which sublimes in four-sided prisms of a brownish white colour. Its composition is $Hg\,Cl$; atomic weight, 235·5.

Mercuric chloride, or corrosive sublimate, is prepared in the same way, but with the omission of the second quantity of mercury; hence, in subliming, it is a mixture of common salt, with sulphate of the red oxide which is operated upon. The formulæ are, therefore, in the first stage the same as in that for the subchloride, after which comes at once the subliming operation as follows,

$$\text{Hg S O}_4 + 2\,\text{Na Cl} = \text{Na}_2\,\text{S O}_4 + \text{Hg Cl}_2.$$

It may also be made by dissolving the red or yellow oxide in hot hydrochloric acid, when crystals of corrosive sublimate separate on cooling in transparent four-sided prisms, which are colourless, and soluble in 16 parts of cold, or in 3 parts of boiling water: and it is far more soluble in alcohol or ether. The operation called 'kyanising' is the soaking of wood in a solution of one part of mercuric chloride in 80 of water. And this is found to arrest the rotting of the wood in a remarkable degree. Hence, also, mercuric chloride is much used for the preservation of anatomical preparations: the fluid, known as Goadby's fluid, being a solution of this salt mixed with bay salt and alum; the mercurial salt being in the proportion of a grain to a pint. Its composition is Hg Cl_2; atomic weight, 271.

There are two iodides corresponding to the chlorides; they are formed by precipitating the salts of corresponding oxides by means of potassic iodide. The subiodide is a green, and the iodide a brilliant scarlet powder. There are likewise two sulphides. The subsulphide is thrown down by passing dihydric sulphide into a solution of a subsalt of mercury. It is resolved by heat into metallic mercury, and sulphide or vermilion.

The sulphide, or cinnabar, constitutes, as already stated, the common ore; in its artificial state it forms vermilion. When dihydric sulphide is passed to saturation through a solution of a mercuric salt, a white precipitate falls; this becomes black, and, when dried and heated in a retort, yields cinnabar. The black and red products are the same bodies, the colour only being affected by heat.

The Chinese vermilion far exceeds all other in quality, and its excellence is supposed to depend in some measure upon the sunny climate in which it is made. The Dutch is also excellent, and hence they were for many years the chief manufacturers of it. But their process, at first kept secret, has been described in the 'Annales de Chimie,' and is as follows:—

Into a polished iron pot of a foot deep by 2 ft. 6 in. wide, they put a mixture of 150 lbs. of sulphur and 1080 lbs. of mercury, stirring the mixture cautiously to prevent too violent action, and consequent loss. Combination of the two produces a black powder. It is next divided into quantities of about 1½ lbs. each, and put into small jars. A set of three subliming pots, placed in a suitable furnace, are next arranged, so that the furnace flame can be made to play over two-thirds of their height; these are heated well red, and then a small pot of the powder thrown into each, and the emptying of the small pots into them is now kept up continuously for some 34 hours. Inflammation follows the throwing in of each one, the flame rising from 3 to 5 feet above the edges of the pots. A quantity thus amounting to about 410 lbs. having been emptied into each, the pots are covered up, and kept heated for a further period of 36 hours, stirring being occasionally employed by means of an iron rod passed through the pot lid. This lid is also put on after throwing in each one of the small pots, as soon as the flame has subsided. The subliming pots are, lastly, taken out and broken, and the vermilion which incrusts their upper portions ground, sifted, washed, and dried.

Dr. Ure gives a process by Kirchoff, which the former says yields vermilion quite equal to the Chinese. It is as follows:— 100 parts of mercury are rubbed in a porcelain dish with 23 of flowers of sulphur, action being assisted by moistening the mixture with some solution of caustic potash. It is next treated with 53 parts of hydrate of potass, and an equal weight of water, warmed up, and again triturated. The water must be replaced as it evaporates, and the operation continued for two hours. After this, and still continuing the rubbing, the whole is to be evaporated to a thin paste, and the heat removed the moment the colour is of a good tint. Even a few seconds too much or too little serve to injure the result; in the first case it will become brown, and in the second the colour is not fully developed. When cold, the mass is washed with a solution of potash, and afterwards with pure water, and finally dried. Messrs. Atkinson, as also some others, now make excellent vermilion in London.

Vermilion is at times adulterated with red lead, and with di-arsenic pentasulphide, at other times with ferric oxide, and even brick-dust; and, when we consider the deleterious character of the former two, it is necessary to be guarded against them.

Neither water, alcohol, the alkalies, nor the mineral acids singly, have any action upon vermilion. But hydrate of potassa heated with it separates its sulphur; and, again, nitro-hydrochloric acid converts it into $Hg\,Cl_2$. Its composition is $Hg\,S$; atomic weight, 232.

Characters of Mercurial Compounds.—1st. If a substance supposed to contain mercury be insoluble, a portion of it may be placed in a hard glass tube, and then covered with a thick layer of dry sodic carbonate, and subsequently heated. If mercury be present, it will be separated, and condense in globules in a cool part of the tube. All mercurial compounds are dissipated by heating only.

2nd. If the suspected body be soluble, a solution of it may be made, and into it a strip of clean copper placed. Mercury will be reduced upon it, which may be polished to a silvery appearance. And if the strip be afterwards heated in a tube, the mercury may be sublimed off the copper.

3rd. Stannous chloride added may at once throw down a grey precipitate of metallic mercury; if it do so, the compound contained mercury in the state of suboxide. If, on the other hand, the precipitate appears white during the addition of this reagent, and before sufficient of it has been added, the mercury was contained as protoxide. The first white precipitation depended upon the formation of calomel, which latter becomes reduced to the metallic state upon the complete addition of the tin salt.

4th. Potash, soda, or ammonia, gives a black precipitate in salts of the suboxide, insoluble in any excess. But if potass give a reddish precipitate, and ammonia a white one, the mercury was in the form of protoxide.

5th. Hydrochloric acid, or chlorides, give no precipitate in salts of protoxide; but throw down white subchloride in salts of suboxide.

6th. If to the unknown solution, dihydric sulphide, or ammonio-hydric sulphide, be added very cautiously, and a black precipitate appears at once, it is due to a suboxide; but if the precipitate is first white, then brown, and at last black, it is from the presence of protoxide. This last, if removed and heated, will sublime as a dark red cinnabar or vermilion. The sulphides of either oxide are quite insoluble in excess of the above precipitants, or in potassic cyanide.

The methods of estimating the quantity of mercury are modified according as to whether it is associated with other metals, or exists alone in the compound under examination.

First. If the body be soluble, a carefully weighed portion is dissolved in water, and into this solution is thrown an excess of stannous chloride, to which a few drops of hydrochloric acid have been previously added. The mixture is then carefully boiled for a few moments, so as not to lose mercury by evaporation. The liquor is next decanted, and the precipitated mercury got into a small porcelain crucible; it is next dried by first absorbing the water, and then using a very gentle heat, when it may be weighed; or better, where great accuracy is needed, dried without heat by placing the crucible *in vacuo* with some sulphuric acid. The presence of silver or lead interferes with this method.

Fresenius * gives a method of universal application. He takes an ordinary combustion tube, 18 inches long, and after closing one end introduces a mixture of sodic carbonate and powdered chalk for 2 inches. Then a layer of quicklime. Then the weighed quantity of the compound under examination is mixed with excess of quicklime, and this is placed in the next 6 inches of the tube. The mixing mortar is then rinsed out with quicklime, and this is put into the next 1½ inch of the tube; then quicklime again for

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* Fresenius, *Quant. Analysis*, 4th Ed. 220.

4 inches, and, lastly, a plug of asbestos; after which the end is drawn out and bent at a right angle. The tube is then tapped on the table to form a space above the material, and next arranged in a combustion furnace, with the bent end of the tube dipping into a flask having water over the bottom, as in the drawing. Heat is then applied by charcoal, beginning from front to back, as in organic analysis; and, finally, the last traces of mercury are expelled by heating the materials put in at the first end. When all has been distilled out, the neck is taken off, and the mercury all collected, washed, dried over sulphuric acid, and not by heat, and weighed.

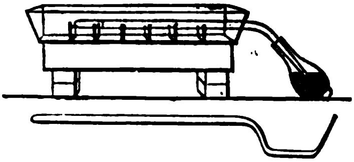

Fig. 31.

An accurate method also is the following one, which is very similar in manipulation. In it the compound is heated with dry lime, being placed, as before, in a combustion tube, but of the shape depicted below the furnace arrangement figured upon the last page, where it will be seen that a chamber is formed at one end to serve as a receiver.

Into this tube a small plug of asbestos is first put close up to the receiver end. Then dry fragments of quicklime, until they reach nearly to the centre of the tube; next the mercurial compound; a carefully weighed quantity of about twenty grains being employed, or ranging from one to two grammes. After this the tube is filled to its front end with more lime. It is next arranged, as in the last case, in a combustion furnace. To the outer end of the tube is connected a small tube from an apparatus for the evolution of dry hydrogen gas. A current of the latter being passed in the combustion tube is heated to redness by hot charcoal, commencing at the end next the receiver, and carrying it back to the outer end. After the full decomposition of the specimen, the evolution of gas is steadily kept up till all watery vapour is driven out; after which the receiver is cut off, and weighed with its contents, and again weighed after thoroughly cleansing out the mercury, when the loss will correspond to the weight of the latter. If nitric acid be present in the compound to be analysed, quicklime cannot be employed, but copper turnings must be used instead.

The methods given all separate metallic mercury, but it may be estimated accurately in a soluble compound, as sulphide. For this the solution is to be acidulated with hydrochloric acid, and excess of dihydric sulphide gas passed in, allow the precipitated sulphide to subside, and then filter, wash quickly with cold water, and dry at a moderately low temperature and weigh.

CHAPTER VII.

NOBLE METALS.

SILVER.

THERE is every evidence of the knowledge of silver from the very remotest ages. Thus, in the book of Job, it is said, 'Surely there is a vein for silver;' and again, in the book of Genesis, we are told that Abraham bought the ground for his wife's burial-place, and, to pay for it, 'weighed out four hundred shekels of silver, current with the merchants;' and, somewhat later still, the Spanish peninsula was extremely productive of silver. In the middle ages Austria was its chief source, in whose mines it was found as an associate metal with lead, and in the varying proportion of from 60 to 600 ounces to each ton of lead. It was also obtained plentifully in Saxony and the Hartz district.

At the present day Mexico, the United States, Peru, and Chili, supply vast quantities of silver; in the former principally from the mining districts of Zacatecas and Guanaxuato.

In Europe, Spain, Austria, Saxony, the German States, and, lastly, our own island, furnish a very considerable quantity, ours being all from lead sulphide, much of which silver was formerly left in the reduced lead; but, since the use of Mr. Pattinson's excellent process for its extraction, this silver has been profitably separated; so that, from this source, in one year alone, viz. 1852, the large amount of 800,000 ounces was obtained. Our average annual produce has since that time been about 610,000 ounces.

Mr. J. Arthur Phillips* gives a table of the production of silver n the principal silver-yielding countries of the world, and from this it appears that the totals obtained in the years 1800, 1850, and 1865 respectively, were, for the former, 2,337,300 lbs. troy; for the middle date, 2,827,425 lbs.; and for 1865, 4,017,000 lbs. Then, calling the latter year's total amount 100 parts, the percentage of the various countries was as follows, viz. Mexico, 42·3 per cent; the United States, 25; Chili, Peru, and Bolivia, 18; Europe generally, 12·2 (of which latter Britain furnished 1·5 per cent); Russia, 1·5; Brazil and New Granada, ·8; Australia and other British possessions, ·2.

Silver is found, first, as native silver, occurring in flat masses, at times arborescent, and often crystalline, the cube and octohedron being the prevailing forms, also the cubo-dodecahedron. Native silver is often associated in Mexico and Chili with iron in ferruginous rocks; whilst in America it occurs with native copper, large masses often being seen to consist of the two metals diffused, although distinct from each other, the silver showing in specks upon the surface of the copper. At Copiapo, in Chili, considerable quantities of silver are found native and in a massive condition.

Native silver is usually free from any considerable admixture with other metals; but it always contains gold, often in mere traces, but never quite absent. But few analyses have been published of native silver. The following one, made and sent me by Professor Church, is interesting as being a specimen from an English mine, Wheal Ludcote, in Cornwall :—

Silver	97·86
Chloride of Silver . . .	·71
Gold and Antimony . .	·21
Iron	·15
Metals precipitated by H_2S .	·10
Loss	·97
	100·00

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* Phillips' *Mining and Metallurgy of Silver*, page 320.

Again, silver is found with sulphur as sulphide, either alone or mixed with certain other metals, viz. iron, copper, antimony, arsenic, and tin. The sulphides may be divided into three kinds, dependent upon these admixtures. First, there is the common sulphide of Mexico, known as vitreous sulphide: this is of a leaden colour, having a glassy, conchoidal fracture, but occurring sometimes crystalline; it is very fusible, and also readily yields its silver by parting with sulphur. It is the most common ore, and is a protosulphide. It is very abundant at Zacatecas and Guanaxuato. Composition, when clean and pure:—Silver, 86; sulphur, 14. But the ordinary working ore is very far from pure, and of these ores Phillips gives the following analyses. The first is one of an ore of 'more than average richness, from the district of La Lux, Guanaxuata; and the second an average sample of ore:'—

1.	
Silver . . .	1·04
Iron . . .	4·71
Copper . . .	0·55
Sulphur . . .	6·79
Carbonate of Lime .	8·25
Carbonate Magnesia .	3·26
Silica . . .	75·00
	99·60

2.	
Sulphide of Silver .	0·15
„ Iron .	26·52
„ Lead .	2·07
„ Arsenic .	0·10
„ Zinc .	5·00
Sulphate of Iron .	0·25
„ Lime .	0·43
Peroxide Manganese .	3·54
Carbonate Lime .	4·18
„ Magnesia .	0·96
Silica . . .	50·00
Moisture . . .	6·80
	100·00

Another sulphide is known as brittle silver ore, which in appearance much resembles the last, except in being of slightly darker colour. This, also, is readily decomposed by heat, and, during decomposition, evolves fumes of arsenic and antimony, the former being recognised when present by its peculiar garlic odour.

This ore is found, not only in Saxony and Hungary, but also in Mexico, Peru, and Chili. Composition :—Silver, 66·50; antimony, 10·0 to 14; iron, 5·0; copper and arsenic, 0·5; sulphur, 12·0.

The third sulphide common in all silver mines, but particularly at Freyburg, is the red silver ore. This is a crystalline ore, often occurring in beautiful ruby transparent crystals, wherein the sulphides are associated with oxides. It contains antimony largely. Composition :—Silver, 56 to 62; antimony, 16 to 23; sulphur, 11 to 14; oxygen, 8 to 10.

Next. We have chloride, and also iodides, bromides, and arsenides of silver. The former, or native-horn silver, is one of the most abundant ores of Chili. It is a true chloride, and, although most commonly amorphous and horny in its appearance, is also at times found crystallized in very small cubo-octohedral crystals. Its colour is yellowish, and capable of being darkened by exposure to sunlight, just as ordinary precipitated chloride of silver would be. If fused before the blowpipe, its chlorine will be driven off, and a button of silver left. Composition ——Silver, 75·3; chlorine, 23·7.

Native alloys are found, and thus an amalgam of mercury with silver exists in many localities. It is silvery white, and often crystallized; at times of a green tint on its surface, dependent on the presence of copper. It is brittle, and, if cut, crackles under the knife. Average composition :—Silver, 36 parts; mercury, 64; up to silver, 86; mercury, 14.

Lastly, what is known as antimonial silver is a natural alloy of antimony and silver, containing 84 of silver to 16 antimony.

Phillips mentions an alloy of antimony and silver of the formula Ag_2 Sb, and containing 77 per cent silver, with 23 antimony.

The Mexican mines are the chief of all the North American ones, Zacatecas and Guanaxuato being the principal.

The sulphides here obtained are almost always reduced by amalgamation by the Patio process, to be described; but about one-fourth of the ores are directly smelted.

At Guanaxuato the mines are very deep; 'Valencia' is no less than 343 fathoms, and is entered by a principal shaft of 30 feet in diameter. 'Rayas,' next in depth, is 215 fathoms.

The ore occurs in primitive rocks, often in calcareous or quartz veins. It is often stained with oxide of iron. Such ores are called colorados by the Mexican miners, in contradistinction to what they call negros, or true black sulphides. Where the ore is exposed to the air, it is generally thus rusted.

They often contain a considerable amount of gold, so as to render their refining a matter of much profit. But, even after refining, I have commonly found left in the Mexican dollars (made from such silver) from 3 to 5 grains of gold per pound troy. Down to some 100 fathoms these Mexican mines are rich, but after that they gradually diminish in produce.

Next to the Mexican mines come the newly-discovered ones in Nevada country, North America, opened in the year 1859, from which an enormous produce of silver is obtained. At one of these, the Great Comstock, Phillips states that 1250 tons of ore are raised daily. The ores are sulphides of various kinds, and argentiferous galena is also found of rich quality, in which the proportion of gold is also considerable. The ore is in a brownish quartz, which, on examination, shows specks of 'finely disseminated gold and silver, and occasionally spots of chloride and sulphide of the latter in it.' Some of the workings are shallow, but some of the shafts are 600 to 800 feet deep.

There are several methods of separating silver from its ores, but they may all be classed under three distinct processes. First may be mentioned a number of operations, which are all methods of uniting the silver of the ore with a quantity of lead, these two being subsequently separated. Secondly, some ores are treated by conversion of the sulphide into chloride, and then reducing the latter into metallic silver, in the wet way; or the sulphides may be converted into sulphate, and then the silver separated from the solution. Then, thirdly, we have the great process, by which the Mexican and Saxon ores have been reduced, viz. amalgamation.

For carrying out the first process, the ores, if rich, are fused with lead or roasted lead ore; thus an alloy of silver and lead is formed, which floats upon an under-stratum of plumbic sulphide, with sulphides of other metals. Ores containing lead, copper, and silver, if the lead be large in amount and the copper smaller, are worked as lead ores would be, and 'workable lead,' fused out while the matts obtained are repeatedly fused with lead compounds, until all the workable lead is separated. This is then cupelled for the silver, as hereafter described, and the matts at length worked by liquation for black copper, and to separate the remaining silver.

Poor ores, containing copper in excess, are smelted with iron pyrites as a flux; thus earthy gangue is separated, and richer matts obtained after several such roastings. These are fused with lead compounds, or with ores which contain lead, and thus workable lead is obtained for cupellation, and the matts worked again till they become so cupreous, that they are worked finally as black copper.

The separation of silver from argentiferous galenas will be described under the article Lead.

Where silver exists in the ore in the metallic state, as at Kongsberg, in Norway, metallic lead fused with it in about equal weight to that of the ore, combines at once, and on cupelling the mixture, about one-third of the silver-lead will come out as silver.

Where other metals contained in silver ores are disregarded, the amalgamation processes are applied, but where it is an object to separate such foreign metals, as where silver is obtained from lead ores, or from argentiferous or black copper, the above or some other operations are practised. Thus, at Mansfeld, for the separation of silver from copper ores, the black copper, as it is called, is mixed with poor lead, equal in amount to 500 times the quantity of silver estimated to be in the ore, and then cast into disks or cakes of about 3 inches thick and 2 feet in diameter. These (weighing about 3½ cwt. each) are subjected to a process called liquation, or sweating, performed by placing them in an appropriate furnace, and then heating. By this the lead runs from the mass, carrying the silver with it, and also small portions of copper, while a mass of spongy copper will remain, constituting the skeleton of the disk, although retaining, at the same time, small traces of lead.

The sweating-out of the lead and silver occupies about three hours; but a small portion is generally retained in the discs, which is subsequently recovered by a second sweating operation upon them at a higher temperature. The above is one of the plans followed, as stated, at Mansfeld for the extraction of silver from 'black copper.' A second will be described under the article Copper. Under the second plan of separating silver from its ores, come the wet methods devised of late years, partly to avoid amalgamating. They are quicker of performance, and, moreover, separate the silver more completely from other metals.

The most simple and economical of these wet plans, suggested by Ziervogel in 1857, was applied by him to the separation of silver from the Mansfeld copper matts, where less than one per cent of silver is associated with 80 per cent of cupric sulphide, and about 11 of ferric sulphide.

The ore is first carefully roasted for about 10 hours altogether, by which the sulphides are oxidized and converted into sulphates; but, by continuous roasting, those of copper and iron will have become decomposed, and oxides of these metals formed. Extreme care, however, is needed to prevent similar decomposition of the silver salt, which would, in such case, be carried to the condition of metallic silver; while, at the same time, the roasting must be carried on so as to ensure the oxidation of the copper and iron completely.

After the roasting, solution is effected, the argentic sulphate being dissolved, while the other oxides are left. The latter are separated, and then the silver reduced to the metallic state by placing pieces of metallic copper in the solution. This process, is, however, unfit for ores which contain any quantity of lead, zinc, arsenic, or antimony; but it is essential that they contain cupric sulphide for the success of the operation.

Before this process was devised, that of Augustin was used, in which the argentic sulphide was roasted first alone, so as to convert the copper and iron into oxides, and the silver into sulphate;

after 8 hours roasting for this, it is removed and ground, then mixed with 5 per cent of common salt, and again roasted for 3 hours with frequent stirring, so as to decompose the salt by means of the sulphates, and chlorinate all the silver. The charge is then withdrawn, and placed at the bottom of a kind of percolating tub, a tub with a second or false bottom; this second bottom after being first covered with a little straw, has a linen filter cloth put over all; upon the latter the powdered matt is placed, and on this is poured a hot and tolerably strong solution of sodic chloride, the latter being a solvent for the argentic chloride present. The filtered solution, thus cleared from insoluble matter, has then plates of copper put in it, which, by taking the chlorine of the argentic chloride, becomes cupric chloride, and the silver is deposited in the metallic state, requiring only washing and compressing, or fusing.

In 1848, Dr. Percy described a method of dissolving silver for its separation by sodic hyposulphite, in which he found its chloride more soluble than in sodic chloride; and some ten years after, Don Patera adopted this menstruum at Joachimsthal for the rich ores found there. His plan, after picking the ore so as to separate poor portions, is to roast them for about 4 hours, passing at the same time a current of steam over the bed of roasting ore. It is next removed and ground, and then mixed with 6 to 12 per cent of salt, and 2 to 3 per cent of ferrous sulphate to decompose this sodic chloride, and then the whole is again roasted, and again with the admission of steam, which assists in the chlorination of the silver, when after about 12 hours the charge is removed for washing.

It is first washed with water in order to remove soluble chlorides and sulphates; after which, the undissolved portions are treated upon filtering tubs with sodic hyposulphite, which dissolves, and carries through the argentic chloride. The solution obtained is then precipitated by sodic sulphide, as argentic sulphide; this is removed, washed, and then heated in a muffle, by which the sulphur is almost entirely got rid of; but it has to be refined from the last portions, by fusion in plumbago crucibles in which some iron is placed; the sulphide of iron so formed is absorbed by throwing some bone-ash upon the surface of the melted metal, and then skimming it off.

The third process, that of amalgamation, is practised in its most primitive manner at the Mexican mines, under the name of the Patio process, from the paved open space in which the chief part of the operation is carried on. It is a plan of some antiquity, having been devised in 1557 by Bartolomè Medina. In Saxony, and also at the North American workings at Nevada, machinery is employed, and the details of the amalgamating process consequently considerably varied. But in all cases, the silver in the ore is first brought into the state of argentic chloride. At Mexico, where fuel is dear, while the warmth of climate affords naturally a higher temperature, the conversion of the argentic sulphide in the ore to chloride, is effected by simple contact of the common salt with the ore. But at Freiberg and Nevada, the conversion is much more quickly effected by roasting the ore with the salt in reverberatory furnaces. Again, at Mexico, where mercury is cheap, the argentic chloride is decomposed at once by it; but in the other works named, the chloride is first reduced into metallic silver by means of pieces of iron, and the silver itself directly amalgamated with mercury in order to isolate it from the great mass of residuary matter. The loss of mercury (always considerable) is thus much less in the European than in the Mexican process.

The details of the Patio operation are as follow:*—After having overlooked all the ore, and cast out all portions which from poverty would not be worth working, and at the same time having set aside any others which from richness will answer for direct smelting, the remainder is broken into moderate-sized lumps, and then taken to stamping-mills. These are a series of iron mortars, in each of which, by an axis with a cam upon it, corresponding to each mortar, a large vertical stamp, or pestle, is lifted, and then dropped; these stamps, weighing about 200 lbs. each, soon reduce the ore to a smaller size, and by sifting out the larger lumps, and returning them to these 'morteros' for a second stamping, the whole is brought to a fit size for grinding. A stamp and mortar of this kind is figured in the article on Gold. It is next removed to the crushing-mills, to be ground fine. These mills, or 'arrastres,' are round cisterns of about 4 yards in diameter; the bottom is formed of pieces of porphyry of about 18 inches long, by 4 square, placed vertically one against the other. The rough texture of this stone assists in grinding the ore, but the grinding-stones of the same material wear rather rapidly away.

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* Much detail of this operation was given to the Author by Mr. J. Napier. Jun., who for a time was a pupil of his before going out as Assayer to the Anglo-Mexican Company.

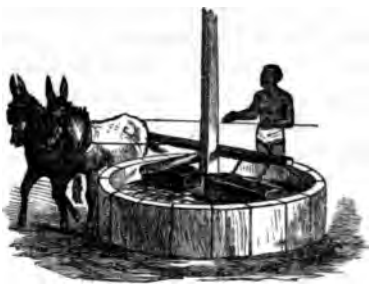


Fig. 32.

From the centre of the mill rises an upright shaft, to which are attached two cross-bars; to these the mules are harnessed, and the grinding-stones tied. These are of porphyry, and are, in length, a little less than the radius of the mill, and about 16 inches thick. By this grinding, which lasts about 24 hours, and which is carried on wet, the ore is reduced to an impalpable powder, which is removed from the mills to a large shallow tank, where it is allowed to remain until the surplus water has evaporated, after which it is removed into a large, paved courtyard, or 'patio,' where it is spread out to the thickness of about a foot, the whole mass to be operated upon weighing about 60 tons. The paving-stones are cemented at the joints to prevent loss of mercury. The patios are sometimes above an acre in extent, and surrounded by a low stone wall. A certain quantity of mercury, or of silver amalgam, is charged into the arrastre in order to take up any associated particles of gold which may have been in the ore; and a solid amalgam is to be used in preference to mercury alone, as the latter, from its extreme fluidity, is very apt to pass into the interstices of the arrastre and be lost. The author remembers seeing put up in London a large mill for crushing gold quartz, in which mercury was also put for the amalgamation; but the mill was found useless, from the fact of the mercury passing through even the comparatively close plates of the bottom, and thus caused great loss.

A quantity of common salt is next mixed with the ore, and the greater the amount, the quicker the operation, but it is usually added, in the proportion of from 3 to 5 per cent of the weight of the ore, after which the mass is well trodden by mules for a few hours, when it is allowed to remain at rest till the following morning, or for about 24 hours. Calcined copper pyrites ('magistral') is then added, to the extent of about 28 lbs. to every ton of ore. This magistral is obtained by exposing copper pyrites (a compound of cupric and ferric sulphides) to the action of atmospheric air for a month or two, after having previously ground and wetted it. Oxidation commenced, it is removed, and roasted for about 8 hours with a small quantity of common salt, constantly stirring the charge. Thus the sulphides are converted into sulphates, and the result is a compound containing on an average about 30 per cent cupric sulphate with 9 per cent ferric sulphate. Now, as in winter, the patio mixture acquires heat more readily than in summer, so, at the former season, less magistral is employed. The whole is again well trodden as before for about an hour, so as to ensure perfect mixture. The mercury is next added in the proportion of from 5 to 6 times the presumed weight of the silver contained in the ore. It is effected in a shower, by pressing the metal through a sheet. Incorporation is ensured by again treading for 5 or 6 hours, and again upon every other day, until the amalgamation is complete, the heating of the mass regulating the amount of treading. The amalgamator watches very closely the progress of the operation, and, by taking assays from the heap every morning, he judges of the state of the amalgamation by washing away the earthy particles from the assay, and examining the appearance of the remaining portion of the amalgam. For this he employs a small bowl, or 'jicara,' taking about

8 oz. of the material for the purpose. The mass having been well trodden, and also turned over by hand every other day, until amalgam is no longer formed, which generally happens in from 26 to 30 days, the operation is considered at an end. The heap is then carried away to the washing apparatus, where the amalgam is separated from earthy matters, &c., by washing; a deep stone vat being employed, through which a constant stream of water is flowing. A shaft working in this, and carrying some agitating arms, keeps the water in constant motion, and consequently the lighter non-metallic particles are kept afloat and washed off, while the amalgam sinks. The former flow into a second and similar apparatus, whence after a second washing they are thrown aside. The shaft is revolved by mules, rapidly at first, but, towards the end of the operation, more slowly, in order to allow the heavier amalgam to subside; and examination is made from time to time to see if this is the case. The feet and legs of the mules employed in treading the torta are also washed at the tanks, to save any stuff adherent to them.

The amalgam itself is cleansed, not by washing alone, but also by treatment with a little fresh mercury; this, stirred with it, separates impurities, so that they may be washed off the surface, when the mass is wiped and put into a strong conical straining bag, formed of canvas, sufficiently strong to contain some 2000 lbs. at a time, the weight of the mass assisting in squeezing out the excess of mercury, and forcing it through the texture of the bag. It is further squeezed in the process of forming it into masses for the distillation operation. These masses are wedge-shaped, with a blunt point, so that six of them, packing together, form a circular disc with a hole in the centre. Each wedge weighs about 30 lbs. A number of these circular discs are piled upon an iron plate, which has a hole in its centre: over this an iron bell, or 'capellina,' is dropped, and luted by its edge to the plate. The bell is massive, and about 3 feet high by 1 foot 6 inches in diameter.

A brick cylinder is next temporarily built a foot all round the hole; this is filled with burning charcoal, and kept supplied and heated for from fifteen to twenty-four hours, during which all the mercury distils off, and, passing down a pipe from the hole in the iron plate, condenses in the water contained in a cistern placed below. The silver is left in a frosted and spongy state, and is known as 'plata pina.' It is frequently transmitted to this country, and from many samples examined by the author he has found quality to average about 994 parts in 1000. It is therefore very near to fine silver.

Phillips gives the following details of the capellina distillation:—Height of the bell, 3 feet; diameter, 18 inches; thickness, 1½ inch. Its charge is about 2000 lbs. of amalgam at each operation, which yields 400 lbs. of silver, and with a consumption of 500 lbs. of charcoal.

The rationale of the Patio operation, although very complex, is in outline as follows:—The ore is a compound of argentic sulphide and chloride; by the addition of sodic chloride and the copper ore, sodic sulphate and cupreous chloride are produced. This latter decomposes the silver ore, and an argentic chloride and cupric sulphide are the result. The argentic chloride is dissolved in the excess of sodic chloride, and on the addition of the mercury it is decomposed; part of the mercury combines with its silver to form the amalgam, while another portion is lost in the operation by being converted into calomel; and again, some becomes so finely divided, and with portions of calomel so mixed up in the residues, as to be the cause of enormous waste in the mercury used.

Amalgamation of richer ores, or those containing much chloride, or native silver, is sometimes quickly effected by mixing the ground ore with water into a thin mud, and then heating them, first with common salt, and next with mercury. The vessel employed is built frequently of stone at its sides, but it is furnished with a copper bottom, which latter is essential in the decomposition of the ore, as it aids in the decomposition of the argentic chloride (or iodide or bromide) contained in it, and brings metallic silver in contact with the mercury employed. Under this copper bottom is a fireplace for the combustion of the wood employed to heat the mixture of ore and water to about the boiling point. This done, salt is added, to the amount of 10 per cent of the ore; after which, stirring is kept up to prevent adhesion to the bottom, and mercury added in successive portions as long as it is taken up for the formation of amalgam, examination of this being constantly made, and the addition stopped as soon as the added mercury does not thicken, but remains fluid.

The amalgam is now recovered and distilled, but the silver got retains a portion of copper with it. The residuary ore material (now poor) is nevertheless added to the ordinary tortas, in order to separate any remaining silver.

In order to concentrate these ores, and thus not to have too great a body of material for heating, they are crushed roughly and washed upon an inclined plane; but ores containing much sulphide are difficult of concentration by such means, as they reduce to so fine a powder, and that of so light a character, as to wash off also, and thus occasion loss. The ores worked by this plan are chiefly those known as 'Colorados,' found in shallow workings, and hence already more or less air decomposed.

The Saxon operation is a more finished one; and as labour, and also mercury, are more expensive, while water-power and fuel are abundant, machinery is there very profitably used, as also quicker plans for amalgamation. The ores worked are those which are found to contain less than 7 per cent of lead or copper; if more was present, it would interfere much with the formation of the amalgam, by combining with the mercury, and so causing loss.

These Saxon ores are sorted so as to average, as near as may be, about 4 oz. silver per 100 lbs., and, in addition to argentic sulphide, contain also sulphides of iron, copper, lead, bismuth, and sometimes arsenic, antimony, and zinc.

About 25 per cent ferric sulphide is advantageous, as sulphur is necessary to set free chlorine from the sodic chloride about to be added. If, therefore, this sulphide be in but small quantity, a sufficient quantity of it, in the form of iron pyrites, is added, the powdered ore being mixed with the latter. Next about 10 per cent common salt; after which the whole is heated in a reverberatory furnace, at first gently, with constant turning, so as to dry it well, the fire being gradually raised. When the first fumes have passed off from the roasting, the chlorination of the ore is started by raising the heat to a bright red, which point is kept till no more gas is disengaged. The ore will then be found to have lost about one-tenth of its weight, and the silver compounds to have been converted into chlorides, with a little metallic silver. The fumes evolved during roasting consist of sulphurous acid, from some of the sulphur oxidised by the air; also arsenical and antimonious oxides, from these metals, when present with the sulphides in the ore.

The associated ferric and cupric sulphides, by roasting, become sulphates. The ferric sulphate (with some peroxide) reacts upon the common salt, and chlorine and hydrochloric acid are set free, which, in turn, react upon the silver sulphide, and convert it into argentic chloride.

Where, as is sometimes the case, the ore contains more than sufficient iron pyrites, a slight preliminary roasting is used to drive off the portion in excess of that needed.

The mixture is then removed, and, when ground, is ready for amalgamation. This operation is performed in stout casks, of about 2 ft. 10 in. long by 2 ft. 8 in. diameter. The wood, in order to stand the friction and wear of the iron to be put into them, is at least 3 inches or more thick; they are strongly hooped, and centred upon axes fixed to each end. They have a large stopper-hole in the usual place in their circumference.

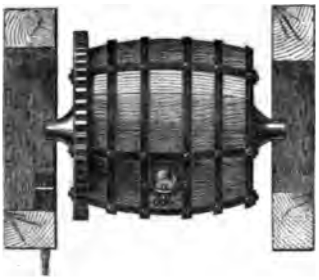


Fig. 33.

A series of twenty of these is arranged in a machine where a shaft worked by water-power is connected by a toothed wheel, *a*, with similar wheels, *b*, placed on one end of each cask, by which means they can be made to revolve upon their axes. By an arrangement of hose-pipe and funnels, *c* and *d*, the charge is introduced to each as follows:—First, about 35 gallons of water; next, half a ton of the ore mixture; and, lastly, 80 to 100 lbs. of iron, in pieces of 1½ inch square by ⅜ thick.

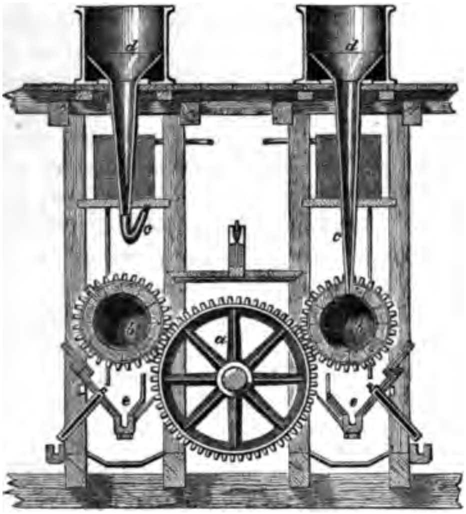


Fig. 34.

The casks are then stoppered up, and by the machine being set in action, are revolved at about fifteen turns per minute for an hour and a half; during which time the iron acts upon the argentic chloride dissolved in the alkaline chloride, and converts it into metallic silver. The motion is then stopped, and 550 lbs. of mercury put into each barrel, by a tube from a reservoir. They are then put in motion again at twenty-two revolutions per minute, and rotation continued for nineteen hours, stopping occasionally to examine the state of the amalgam forming. The temperature gradually rises, and may be somewhat controlled by the rate of revolution, a temperature of 90° F. = 32° C., being the most advantageous.

At the end of this time the amalgamation will generally be found completed. The barrels are then stopped, and nearly filled with water; next revolved slowly so as to collect the amalgam, and they are then turned so that the stopper of each is downwards over the discharging troughs *e*, which run throughout the machine, the stopper removed and the contents allowed to flow away, and mechanical separation is then effected between the actual amalgam, portions of uncombined mercury and the muddy residue.

In the first action in the casks the iron decomposes the argentic chloride, and also other metallic chlorides present. Any metallic copper reduced from its chloride at once reduces silver from its chloride. This silver is immediately taken by the mercury. The reason for putting the mercury into the barrels after some time of revolution, is, that the silver may have been reduced, and other metals be in such condition, as that their chlorides may not act on the mercury, with the formation of calomel, and consequent loss. This would be especially the case, if introduced before the ferric chloride has been reduced to the state of ferrous chloride.

The amalgam, which, in addition to silver, contains also portions of other metals which were in the ore, after straining and pressure is next submitted to distillation, in an apparatus similar to the one shown in fig. 35. It consists of a series of brick furnaces, two of which are here given, the left-hand one closed as in operation, the right shown in section; this will be seen to consist of the following parts:—First, at the bottom an iron drawer containing an iron basin, upon this is placed a large iron bell, in which stands a strong tripod, also of iron, carrying five flat dishes; the casing round the upper part of the bell, forming a fire-chamber, has a door in front for feeding with fuel, as seen in the closed furnace, and an iron cover to slide over the top opening.

Now in operating, the dishes are first charged with about 60 lbs. of amalgam in each, the basins are then filled with water, and the bells lowered down over the dishes; next, the vacant space between the upper part of the bell and the furnace is filled with turf and charcoal, lighted, and the heat gradually got up to its maximum in about seven or eight hours; after which it is slowly lowered, great care being taken in this firing, for if the heat be too great, silver, being slightly volatile, will be carried away with the mercury; and if, on the other hand, it be not high enough, some mercury will be left with the silver: but as the mercury distilled off, as well as that filtered away at first, are employed over and over again, of course any retained silver is not lost. The first strained mercury retains about ·5 per thousand parts.

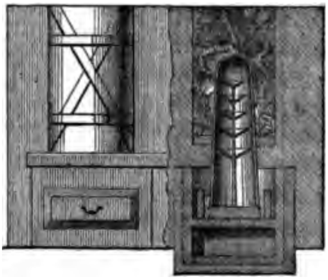


Fig. 35.

The amalgam contains on an average about 84 per cent of mercury, with 11 per cent silver, the remaining 5 per cent being composed chiefly of copper, with traces of tin and lead. While the silver remaining after distillation contains about 75 per cent pure silver, with 25 per cent copper and other metals. Lastly, the earthy residues of the amalgamating operations afford small quantities of amalgam, which by distillation yields a yet coarser silver.

It is said that the apparatus above described does not completely separate the silver and mercury; and that loss is often occasioned by the cracking of the bells; and hence, at some works an iron retort is formed by a crucible shaped body, upon which a head is fixed so as readily to remove; from the side of this head a wide arm passes out into an iron condensing tube, kept cool by passing through a cistern of water, and ending in a square receiver for the distilled mercury. A plate of iron is put into the centre of the crucible part of the retort, the whole interior is coated with lime, and the charge of about 4 cwt. of amalgam introduced. A slow fire is got up, the mercury distils off, and the silver adheres to the iron plate, with which it may be removed when the operation is over.

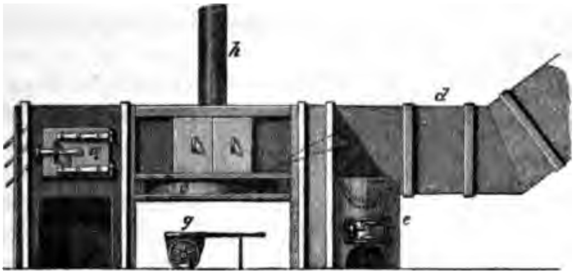
The poorer ores at Nevada are not worked by the barrel process, but in amalgamating pans upon the principle of those which will be described for gold. These silver ores, although poor, commonly contain gold of value equal to about half that of the silver present. They are first stamped, and, for the collection of this gold, mercury is put into the stamp mortars, equal in weight to the expected weight of gold, whereby the latter is obtained as a hard amalgam with the mercury, adhering to the parts of the stamp mills, whence from time to time it is removed.

The finer parts of the ore are next washed off; the water containing them, after being allowed to deposit, is run off clear, and the remaining mud run into the amalgamating pan. The mullers are then set in motion, so as to complete the grinding begun in the stamping mill. The temperature is now raised to 200° F. =93° C., by means of steam passed in. Next from 10 to 15 per cent of mercury is squeezed in a shower through the texture of a canvas bag. At this time also a little cupric sulphate, or sometimes a little sulphuric acid, is also added to assist in the amalgamation. Rotation is then kept up for 3½ hours, the temperature also being kept as near as possible at the point named. Water is then run in, so as to flow off the pulp into a separator, where the earthy matters are washed off the amalgam. A certain portion of pyrites also remains with this. The amalgam is then strained, and the excess mercury separated as much as possible before distillation. This latter is effected in a retort very much resembling one of the Lansberg mercury retorts in all its details, for the retort is of cast iron and about 3 feet long by 1 foot diameter; but the outlet pipe passing from its back is surrounded by a condensing tube of cold water, before passing into the receiving vessel. This is for the more effectual condensation of the mercurial vapour. The amalgam is introduced into the retorts in iron trays; these are covered with a lute, either of very thin clay or of lime, to prevent adhesion of the silver remaining on them.

Phillips says that the 'best results obtained by the pan process rarely amount to 75 per cent of the assay value of the ore; the average will scarcely exceed 65 per cent.' 'The tailings from the pan process, after having been exposed to the atmosphere for a few months, may sometimes be again advantageously worked over, thus increasing the total produce to about 85 per cent; but it is only under favourable circumstances that this can be done.'

The operations practised for the preparation of commercially 'fine silver' are varied, dependent upon the quantity of coarse silver to be operated on. Thus, in the refinery, where very large quantities are worked, the operation of cupelling the silver (or silver lead) is much practised; or where the fine silver is to be obtained as a residue from what are called parting operations, as in the refining of gold, a precipitation of the silver from an acid solution is effected by means of copper; but where, on the other hand, small quantities are operated upon, as in the laboratory, it

Fig. 36.



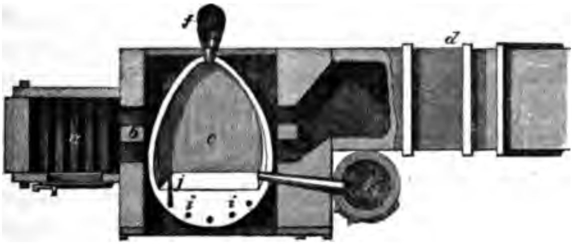


Fig. 37.

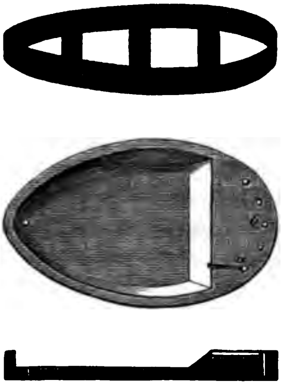
is usual to form a chloride of the silver, and then to reduce the latter,—such practice being found to afford a certain means of separating some associated metals, and hence to afford a finer product than can be obtained by the larger processes of the refinery, although it is by no means uncommon to meet with silver obtained by cupellation very nearly, if not quite, pure.

The process for the cupellation of silver on the large scale is performed in a reverberatory furnace, constructed with especial regard to the nature of this operation, but varying in form in different countries where it is employed.

The ordinary English furnace is represented in elevation in fig. 36, and in plan in fig. 37. A is the fireplace, usually of about 2 feet square; at the back of this is the bridge, *b*, beyond which the cupel, *c*, is fixed. This last is a large dish-shaped vessel formed of some porous material, usually bone-ash, thus affording a texture which admits of the absorption of some small portions of the fluid oxide of lead formed during the operation. The quantity absorbed by the cupel, however, bears but a very inconsiderable proportion to the amount formed in these large operations, which is almost all of it blown off the surface. The object desired by the use of bone-ash is not absorption, but the employment of a material which will admit of long contact with the molten litharge without suffering any corrosion or softening. The cupel or test is made in a foundation formed of a ring of iron (fig. 38), of from 4 to 6 inches deep, and full half an inch thick. This is further strengthened by strong iron cross-bars, which also maintain its shape. It is oval, and varies from 2 feet by 1 foot 6, up to 4 feet by 3 in dimensions. Into this mould the ash is put. The mixture used is chiefly coarsely-ground bone-ash, to which a small quantity of wood-ashes is added. These are wetted with water containing a small quantity of pearlash; and the requisite quantity is packed firmly in the ring and beaten down with wooden rammers, a centre cavity being formed, partly by beating and partly by shaping with a trowel, so that the material is not above 1 inch thick in the centre; a broad rim is formed all round the edge of about 3 inches in width, increased, however, in the front or breast to 8 or 9 inches; at the front or circular edge of which the holes (*b*, fig. 39) are bored for the flowing off of the litharge. When working, a channel or gate (*a*, fig. 39) is cut from the bed to the first hole; but as the litharge, in flowing off through this channel, gradually wears it away, so that the molten silver-lead would run out also, the refiner, when this is the case, stops up this passage, and cuts a new one in the breast to the second hole, and again a third or more if necessary.

Fig. 40 is a section of a cupel through one of the litharge-holes and the gate leading to it.

The cupels so made are allowed to stand some weeks in the warm atmosphere of the furnace-room to dry gradually; when required for use one is slid into its position in the furnace by the under opening, as seen in the elevation (fig. 36), and then securely fixed in its place by an iron wedge, shown on each side. This under chamber is left thus open for this purpose, and also to admit of the carriage for the reception of the litharge, and afterwards of the cupel contents being delivered into it. It is mounted on wheels, so as readily to draw out and in for the purpose.


Figs. 38, 39, 40.

When the cupel has thus been wedged up to its proper position for the right action of the flame, and also of the blast upon it, a slow fire is lighted and gradually raised, lest the too sudden heating should crack it; but much depends, in this respect, upon the cupels not being used green and unseasoned, but well consolidated and freed from moisture by the slow, gradual drying before stated. They are then said to be 'ripe.'

Now the rationale of the operation to be performed in this apparatus is the conversion into oxides of all oxidizable metals associated with the noble metal silver, under the influence of a

current of air passed over the surface of the bath of melted metals, hence the reason for the shallow make of the cupel itself. For this is the property which characterises the noble metals, viz., that, when heated to fusion and exposed to a current of air, no oxidation of them takes places; while, on the other hand, any alloy of base metals will be thus perfectly oxidized, and may consequently by proper management be thus effectually separated. The lead being first oxidized, then gives up again some of its oxygen to metals, such as copper and the like, which are less readily acted upon directly; the lead so set free being reoxidized by the blast.

Refined silver, by cupellation, is then usually obtained from rich argentiferous lead, some lead being so called from its containing silver in very large proportions (no lead being absolutely free from silver), and the operation is thus carried on:—At the side of the cupelling furnace, and over a separate fire, is set a cast-iron pot *e* (figs. 36 and 37); into this some of the silver lead is put and fused; the cupel having been already sufficiently heated, a quantity of the fused metal is ladled into it by a shoot shown as leading from the pot to the cupel. The fire in the reverberatory itself is made to traverse the surface of the metal, its draught being effected by the flue *d* into which the products of combustion pass. Volatile matters and fumes are further carried off by the separate flue *h*. The silver lead being in, the heat of the cupel is next raised, and after the first drossing of the surface, the oxide fuses, and the surface of the bath becomes clear, or, as it is said, uncovered. A large pair of bellows or a fan-blowing apparatus is then set to work, its blast being conducted upon the cupel at a point, *f*, just on the opposite side to the breast-hole already spoken of. This blast keeps up the oxidation of the lead, as by circulation fresh and fresh portions rise to the surface; while at the same time it serves to blow off the litharge by the breast-hole, whence it is collected for subsequent reduction again to the metallic state. The progress of the operation can be examined occasionally by sliding open the doors shown in the elevation. Lead is from time to time added as the quantity working diminishes. Thus the level of the surface with regard to the blast is kept uniform.

It is thus added until in one of the larger class of cupels, some 14 to 15 tons of rich lead have been introduced. The under part of the cupel is then bored, and the rich metal allowed to run out into an iron pot wheeled below for this purpose, the hole so made being again stopped with fresh ash, when a new charge is to be introduced. Ultimately when several of these operations have been performed, and thus a number of cakes collected, they are all added together, and a final cupellation carried on, the first operations being for the concentration of the silver in the lead, and hence this is drawn off as described; the final cupellation of the cakes being for the purpose of entirely getting rid of the lead by oxidation, and thus leaving a cake of pure silver only. The general principle, objects, and results of the operation being much the same in the miniature cupellation for assaying purposes, it will be again alluded to and further described.

From numerous examinations of the quality of the fine silver so obtained, the author finds that the average fineness is about 998 parts in the thousand; and frequently, where the operation has been carried on with more than ordinary care, the quality will reach 999·5 parts in a thousand, and rising at times to nearly or even quite fine silver.

The second operation upon the rich lead lasts about twenty hours, and requires much attention as to blast and general management of the cupellation. It is always made thus a separate operation, in order to avoid loss of silver; for as the metal enriches, the portions of litharge last separated are correspondingly rich in silver; the proportion of silver thus blown off varies, being influenced by the temperature at which the work is carried on, and also by the force of the blast; consequently, such portions found in this second operation are reserved for the separation of this retained silver.

Cupellation is the final operation by which all the silver obtained in Great Britain from lead or its ores is ultimately separated; and if such lead be rich may at once be resorted to; but if, on the other hand, the lead be poor, then some concentrating process is first employed, such, for example, as the one known as Pattinson's process, which will be detailed in the section upon Lead.

The cupellation process on the Continent is carried out in circular hearths, heated on the reverberatory principle. They are formed of brick, and the bed or cupel is a layer of marl or some clayey material mixed with wood ashes. A kind of test is thus formed by beating them firmly into shape upon a brick bed. It lasts, however, but one operation, and is then broken up for smelting, in order to recover the litharge with some silver retained in it. The hearth is covered during the operation by a dome made in iron, but lined with fire lute. This dome is suspended so as to be readily removable.

Properties of Silver.—Its colour is a perfectly pure white, and with much lustre, which is exhibited also when the metal is in fusion. When finely divided as when obtained by precipitation, it has the appearance of a metallic, sandy powder, of a greyish colour, and such powder may be partially welded by cold hammering. Such silver is often crystalline, macle crystals of cubes and dendritic forms being frequent. Silver after fusion may also be artificially crystallized in cubes. It is a very ductile and malleable metal, one grain may be drawn into 400 ft. of wire, and it may also be hammered into leaf as thin as 0·00001 of an inch.

Silver fuses at 1873° F. = 1022°·7 C., and during fusion absorbs oxygen, of which gas it will take up about 22 times its own volume, but at the moment of solidification it expands considerably, and at the same time parts with the mechanically mixed oxygen. This latter taking place after an external crust has formed over the liquid metal, will often burst the crust, and throw out jets of the yet fluid metal, producing the phenomenon of spitting, or vegetation, as it is called. This may be prevented by sprinkling charcoal-powder on the melted metal, which will then quietly withdraw the gas; and it is said that 1 to 2 per cent of copper with the silver will also prevent it. Matthiesen attributes the absorption of oxygen to the formation of an actual chemical compound of silver and oxygen, capable of existing at high temperatures, but decomposing on cooling and solidifying. And this opinion appears probable from the fact that silver must be kept a considerable time in fusion, in order that any great amount of oxygen should be thus taken up. If silver be exposed to a very high temperature while in the state of fusion, it volatilizes very considerably.

Silver is not acted upon by oxygen, hence the tarnish of silver does not depend upon oxidization; it is the result of its strong affinity for sulphur: thus the smallest quantity of sulphuretted hydrogen in the air will immediately be detected by silver. This blackened surface may be readily cleansed by plunging the silver into a solution of potassic manganate, also by washing with a solution of potassic cyanide. What is called 'oxidized silver' (used for ornaments) is really nothing of the kind, but is silver whose surface has been superficially tarnished by sulphur. The articles to be 'oxidized' are boiled in a solution of potassic sulphide, a portion of which is decomposed, its sulphur combining with the surface silver. Hydrochloric acid only acts upon silver when the finely divided metal is boiled in it, and even then but slightly. Sulphuric acid only by boiling the metal in it when sulphurous acid is evolved, and argentic sulphate formed. But nitric acid, especially if slightly diluted, dissolves it very rapidly, forming argentic nitrate. Dihydric sulphide acts upon it even cold. If a piece of silver be put in this, it is decomposed, and argentic sulphide formed upon the surface.

The specific gravity of silver ranges from 10·43 to 10·53 according to its state; viz. whether simply fused or hammered, the latter operation of course condensing it. Its atomic weight is 108, and its symbol Ag.

Compounds of Silver.—*Oxides.* A suboxide or argentous oxide was first obtained by Mr. Faraday, who formed an ammoniacal solution of the protoxide, and exposed this to the air; thus a black film appears upon the surface, which by examination was found to be composed of two proportionals of silver, united with one of oxygen. Wohler obtains it by passing a current of hydrogen gas over argentic citrate previously heated to 212° F. The compound formed is dissolved in water (in which, however, it is not readily soluble), and to this solution potash is added, which throws down the suboxide. But it is by either method a very unstable compound.

The protoxide, or argentic oxide, is the more important one, as forming the base of ordinary silver salts. This is obtained as a greyish brown powder, on adding caustic potass, or baryta water, to a solution of argentic nitrate. This powder is removed, washed, and dried. Gregory forms it by boiling freshly precipitated, and still moist argentic chloride in caustic potass. Argentic oxide will not be precipitated by ammonia, and if we digest the oxide precipitated by potass in ammonia, we get a very explosive compound formed, viz. fulminating silver.

Argentic oxide is slightly soluble in cold water, giving an alkaline solution, and it is readily soluble in acids forming silver salts. It is decomposed by exposure to heat somewhat below redness, and it is said also that solar light will decompose it. Its composition is Ag_2O; atomic weight, 232.

Peroxide of silver has been obtained by Ritter by electrolysing a solution of argentic nitrate. It was thus deposited in black acicular crystals at the positive pole.

Chlorides.—A subchloride, argentous chloride, is said to be formed by exposing ordinary argentic chloride to light, or by exposing silver-leaf to the action of ferric chloride, thus a black chloride is formed; but its nature is not well ascertained.

The ordinary argentic chloride (found native as horn silver) is prepared by adding hydrochloric acid, or a chloride to any soluble salt of silver. In this way we get a curdy precipitate formed, which is perfectly insoluble in water, nitric acid, or dilute acids. It is dissolved by strong hot hydrochloric acid, also by digestion in alkaline hyposulphites, or chlorides, or in ammonia. From the latter it is readily reprecipitated by even comparatively weak acid, as acetic; while from its hydrochloric acid solution the addition of water suffices to throw it down. But it is precipitated from the latter also, by slow cooling in small octohedral crystals. Similar crystals are also obtained when we expose an ammoniacal solution of argentic chloride to the air, for the ammonia is evolved gradually, with formation at the same time of these crystals.

If a solution of argentic chloride in ammonia be boiled, fulminating silver will be formed. Argentic chloride is readily fusible, forming a reddish liquid, which is somewhat volatile; on cooling it becomes a horny mass. If fused with potassa, soda, or their carbonates, it is decomposed into silver, and chloride of the alkali, oxygen gas, and water being evolved. It fuses somewhat under 500° F., or 260° C.

If heated on charcoal before the blowpipe, it yields silver, and emits an odour of hydrochloric acid. On adding a little sulphuric or hydrochloric acid to moist argentic chloride, and then immersing a portion of any easily oxidized metal in it, the chloride will be reduced, the reducing metal being at the same time dissolved.

Argentic chloride blackens in the light, and very rapidly in the direct rays of the sun. If such light-altered chloride be treated with ammonia, it will be dissolved, but leave a small quantity of a black powder, the subchloride above described, but said by some chemists to be metallic silver. Composition, $Ag\,Cl$; atomic weight, 143·5.

Argentic iodide, and also bromide, are found native, but both may be formed artificially, for the first potassic iodide, and for the second potassic bromide, is added to a soluble salt of silver. Both are of a yellow colour, the iodide being insoluble in ammonia; one or other of these salts forms the basis of most photographic operations.

Argentic sulphide is the common ore. It may be formed by heating plates of silver with sulphur. In the moist way it is precipitated by adding dihydric sulphide, or ammonio-hydric sulphide, to a solution of a silver salt. It falls in dark brown flakes which become black upon drying. Upon heating it in the air, it is resolved into sulphurous acid and silver. Fused with iron it yields ferrous sulphide and silver, or with lead, plumbic sulphide, and an alloy of lead and silver. If fused alone it yields a dark-grey crystalline mass on cooling. Composition, $Ag_2 S$; atomic weight, 248.

The more important salts of silver are the nitrate, sulphate, and carbonate. The nitrate forms the lunar caustic of the surgeon, and is obtained by dissolving silver in nitric acid. If heat be used, the solution is somewhat rapid, and attended with copious evolution of nitrous gas; upon cooling the salt will be deposited in large tabular crystals belonging to the right prismatic system. These are to be again dissolved in distilled water, and recrystallized. Copper, if contained in the silver, will impart a slight green tint to the solution in acid, and any gold will remain undissolved in the form of a brown powder. If we have to prepare it from impure silver, the best method of proceeding is to dissolve the metal in nitric acid diluted with not less than three times its bulk of water. The solution is next to be poured off undissolved gold, which is almost sure to be present in greater or less amount. Hydrochloric acid is next added in excess so as to precipitate all the silver as chloride; this is to be separated and well washed, and then boiled with potash ley; by this means it is converted into argentic oxide, which when washed may at once be dissolved in nitric acid, and crystallized.

In commerce this salt is often fraudulently adulterated with plumbic, potassic, or even with sodic nitrates.

Argentic nitrate is soluble in an equal weight of cold, and in about half its weight of boiling water. The crystals fuse readily, and solidify into a white fibrous mass; thus it is commonly cast into small sticks or cakes. It does not blacken by light unless organic matter be present; so in marking inks, of which it forms the basis, the blackening of the writing is assisted by this action of the organic matter of the linen.

If fused in iron vessels it is decomposed, even if no water is present; and copper will reduce silver from the dry salt at ordinary temperatures, by exposing the two to air. From its solution the silver is readily reduced either by copper or mercury. Its composition is $Ag, N O_3$; atomic weight, 170.

Argentic sulphate may be formed by boiling precipitated silver or silver filings, in sulphuric acid, or by adding sodic sulphate to a boiling solution of argentic nitrate. The salt crystallizes in small white shining crystals, which belong to the right prismatic system. They are rather insoluble, requiring 87 parts of water for solution. This salt is often found as an insoluble residue on dissolving the nitrate where the latter has been prepared with impure nitric acid, that is, with acid containing traces of sulphuric. Composition, $Ag_2, S\,O_4$; atomic weight, 312.

Argentic carbonate is thrown down as a white powder on adding potassic carbonate to argentic nitrate solution; it blackens by light, and is readily decomposed by heating.

Amalgams.—Mercury and silver when brought together unite readily, but complete union of mixtures of the two, if attempted cold, only takes place after some weeks of contact, and the mercury must be largely in excess. Therefore, the best method of forming them consists in gently heating the mercury, and then adding silver in a pulverulent form, or as filings. If in this way 8 parts of mercury be mixed with one of silver, we get a crystalline soft amalgam, which crackles between the fingers; the structure of the crystal is prismatic, and it is very white. Indeed, an amalgam, which is at first smooth and pasty, will, by keeping, become crackling and crystalline. This is, in fact, very nearly the composition of the amalgam formed in the Saxon amalgamating work, Kersten's analysis of which shows an average of 84 parts of mercury to 11 parts of silver. Heated to redness, these amalgams give off the mercury, but silver may retain traces of mercury even after such heating. Native amalgams have been found, wherein the mercury and silver are united in atomic proportions. Three such have been described of the following proportions: 1st. One proportional of mercury to six of silver. 2nd. Two proportionals of mercury to one of silver. 3rd. Three proportionals of mercury to one of silver.

The description of the preparation of pure silver has been purposely deferred until now, in order that the above silver compounds should be described previously. To prepare it in the wet way coarse silver is dissolved in nitric acid somewhat dilute; when all is dissolved but associated gold, a further quantity of hot water is added, and the whole allowed to stand until the gold has completely subsided; the argentic nitrate solution is then to be syphoned or poured off carefully, and an excess of common salt added so as to precipitate all the silver as chloride. After subsidence, the acid liquid is decanted, and the chloride well washed with repeated quantities of hot distilled water, until the latter is free from acid. The chloride is then acidulated with hydrochloric acid, added in the proportion of about one pint to each ten pounds of chloride. Into this mud a number of plates of clean wrought-iron are put. A copious evolution of hydrogen is at once set up at the surface of the iron, and the solution of the latter commencing the argentic chloride adjacent to the slips is reduced, and this reduction will spread from each slip of iron throughout the whole, which will thus become a spongy mass of silver. The silver should not be disturbed till all is reduced, or portions of chloride are apt to escape reduction. When all traces of chloride are gone, the iron undissolved is carefully removed, the mixture of ferrous and ferric chloride solution poured off, and the whole mass covered with a quantity of hot water, to which about one-tenth its bulk of pure hydrochloric acid is added. After standing a few minutes, this is poured off and renewed; and after the decanting of the second portion pure hot water is added; and, lastly, the whole is washed, as quickly as possible, with repeated quantities of hot water, until the washings will not render a dilute solution of potassic ferrocyanide in the smallest degree blue. The silver is then squeezed by the hands, and dried in a porcelain basin. If this process be carefully carried out, it will give a product as fine as 999·7 parts in 1000, that is to say, containing only $\frac{3}{10000}$ths of admixture, which latter is due to traces of iron.

A sheet of copper placed in a solution of argentic nitrate will also precipitate it in a crystalline form, and tolerably pure; the product should be cleansed by digestion in liquid ammonia, previous to melting it, but this operation will not give so pure a product as the one just detailed.

But perfectly pure silver can be prepared only in comparatively small quantities, and by fusion of pure chloride with reducing agents. Thus the chloride may be mixed with one to two parts of dry sodic carbonate. This was the old method, but there is during decomposition a copious evolution of carbonic acid, which by swelling the mass in the crucible, is very apt to occasion loss; and again, the fused chloride and alkaline carbonate are sure to be absorbed by the substance of the crucible. Hence, F. B. Miller advises filling the pores of a crucible with a hot saturated solution of borax. When dry, such an one was filled by him with argentic chloride and submitted to a high furnace temperature for 25 minutes, and no absorption was found to have occurred. The cake weighed the same after as before the operation. The use of chalk, as an infusible carbonate, was advised by Guy Lussac. The late Dr. Miller thus employed a mixture of 100 parts of argentic chloride, 70·4 of calcic carbonate, and 4·2 of charcoal; this is heated to dull redness, and kept so for half-an-hour, after which on raising it to a full red, carbonic acid and carbonic oxide are evolved, the calcic carbonate is converted into calcic oxy-chloride; and below this slag is found a mass of pure silver.

But Miller also first carefully prepared his argentic chloride by dissolving any ordinary silver in nitric acid and then precipitating argentic chloride by sodic chloride in excess. The precipitate was well washed, and then acidified by sulphuric acid, and reduced by zinc. Decomposition being complete the reduced silver is next digested with dilute sulphuric acid, in order to remove any basic salts of zinc. Next washed with water, redissolved in nitric acid and precipitated by pure hydrochloric acid. Then the argentic chloride so obtained reduced as before described by calcic carbonate. Some specimens given to the author by Miller were examined, and found to be perfectly pure.

Gmelin gives a very good dry reducing process devised by Mohr, wherein the latter advises resin as the reducing agent. A mixture is made in the proportion of three parts of dry argentic chloride to one of powdered resin. This is packed in a crucible so as to half fill it. A gentle heat is first applied; by this the resin inflames, burning with a green flame; the heat is then raised to the melting point of the silver, the pot opened and a little borax added; on removing the pot, it should be gently tapped on the bottom, so as to accelerate the union of the silver into a mass, which will take place under a layer of charcoal, which latter will be quite free from silver.

The silver obtained by either of the above operations only requires further to be melted, in order to get rid of some adherent impurities, and obtain it in convenient form. These objects are effected by simple fusion with appropriate fluxes, and a slight digression may here be made to describe their action and nature generally. The term flux is derived from '*fluo*,' I flow, and is applied to a class of bodies used in metallurgic operations, either to assist or induce the fusion of a metal, or else when melted to cause the globules to run together from their diffusion throughout a heterogeneous mass of foreign matters by the cleansing effect of the flux on their surface; and they may also effect this latter purpose in a secondary way, by taking up matters with which the metal was combined, whereby its isolation is brought about. As, for example, when we fuse gold quartz with sodic carbonate. The quartz or silica acts as an acid to the soda salt and combines with it, setting free its carbonic acid, and at the same time separating it completely from the gold which it held mechanically.

Again, a class of offices may be performed by them more in the way of reagents than truly as fluxes. For example, they may decompose a body into which a metallic oxide enters, and so setting free the oxide bring the latter within the reducing agency of charcoal. Thus some metallic silicates may be reduced readily.

The following may be enumerated as the fluxes of most common application, and their uses may be thus defined: —

1st. Borax. This is of almost universal application. The salt is best fused so as to drive off its water of crystallization, and the glassy mass obtained is to be powdered. It forms fusible compounds with silica and bases. At high temperatures it combines with metallic oxides, while at lower it will take up foreign matters generally so as to set the metal free and so cleansed upon its surface as to run readily together to form a button.

2d. Sodic Carbonate. This is to be preferred to potassic carbonate, from the former not being deliquescent. This should be fused. It decomposes silicates, as already instanced, and easier when charcoal is present. It forms fusible compounds with metallic oxides, and decomposes some chlorides, as argentic chloride, for example.

3d. Potassic Nitrate, when used as a flux, and heated, loses oxygen and becomes nitrite. Its action is energetic from the quantity of oxygen it contains, and this action is increased where silica is present. Thus it is used to purify noble metals as an oxidator to metallic impurities.

4th. Common Salt, or Sodic Chloride, powdered and heated (to prevent its decrepitation), is often added to a body which induces much ebullition, so as to check the latter and protect the substance operated on from the action of the air.

5th. Black flux is an intimate mixture of potassic carbonate and charcoal, formed by burning 3 parts of argol (crude-potassic bitartrate), and 1 of nitrate together. It forms a good reducing agent, and assists in the fusion of substances. The uses of argol are the same as that of black flux. These are more especially useful in the smaller operations of the experimental laboratory.

6th. Silica, lime, and alumina, are employed; the former in order to withdraw certain bases by forming fusible silicates with them; the two latter to assist in the fusion of those silicates which by themselves would not be easy of fusion. Indeed, the two latter bodies are generally applicable, as all simple silicates are very difficult of fusion.

7th. Plumbic, Cupric, and Ferric Oxides. Of these the former is the chief. It is much used in operations upon silver ores, where we desire to form an alloy of the silver contained in the ore, with lead derived from this added oxide. Hence we employ the first, or litharge, and where the ore does not contain enough of sulphur, or other reducing matter, to set sufficient lead free, we add some reducing agent, as argol, to effect this. Then, on the other hand, as it is advisable not to have too large a mass of silver lead to cupel subsequently, we are at times obliged to add to such a mixture of ore and litharge a certain quantity of nitre (potassic nitrate), which latter counteracts to sufficient extent the reducing agency of the ore itself, by reoxidizing some of the lead reduced during the operation. The use of the two latter oxides is very limited. The late Mr. R. Warington proposed to apply that of copper to gold containing metals which render the latter brittle, the cupric oxide is reduced and affords oxygen to the metal to be separated, while the reducèd copper alloys the gold to a corresponding extent. Ferric oxide is used as a flux for silica, but its application is very limited.

To these chemical fluxes we may add one much employed as a mechanical one, namely, bone-ash. This, by its absorbent quality, is very useful to suck up other fluxes from the surface of a fused mass of metal, and for this purpose it is customary to cover the metal with it, and skim it off just before casting the ingot. It acts just as a sponge.

Having stated thus much with regard to fluxes, the use of such as are applicable to the melting of a quantity of silver obtained by the wet method of reduction just described, may be now examined.

As the impurity likely to lower the standard of this silver would be derived from the iron chlorides, the flux to be first employed would be potassic nitrate, which, by its oxidizing effect, would oxidize the last traces of iron. Therefore about 5 per cent of nitre is employed. Secondly, some borax is added, which will, at the high temperature used, dissolve the ferric oxide. And, lastly, a covering of bone-ash, used just before pouring, will absorb the fused borax, and with it the ferric oxide, leaving the silver clean.

In all melting operations the heat should be of such amount as to render the metal thoroughly fluid, and allow of good circulation in the fused mass; and if this be true of pure metals, it is especially so where any alloy is to be diffused uniformly through the bulk melted.

The tests for the presence of silver are the following:—

1st. If to a solution supposed to contain silver only, we add dihydric sulphide, or some ammonio-hydric sulphide, we get a black precipitate of sulphide, insoluble in dilute acids, alkalis, or potassic cyanide; but boiling sulphuric acid will dissolve it, and at the same time separate its sulphur.

2nd. Potash or ammonia precipitates a brown oxide, insoluble in potassa, but soluble in ammonia; and this solution, on exposure to air, will deposit fulminating silver.

Ammonia salts prevent this reaction.

3rd. Hydrochloric acid, or chlorides, precipitate white argentic chloride; even when 1 part of silver is dissolved in 200,000 times its weight of water, we get opalescence. Light changes this precipitate to a violet black, and, as already stated, it is an undetermined question whether the decomposition so effected by light is due to the formation of a subchloride, or to the separation of silver in a finely-divided state. A trace of mercurous chloride in this precipitate will prevent the discoloration.

The precipitate is soluble in ammonia, from which solution it is reprecipitated by acids. It is insoluble in nitric acid. By heat it fuses to a horny mass.

4th. Silver compounds, when heated on charcoal with sodic carbonate before the blowpipe, and in the inner flame, give a clean and bright bead of metallic silver. The charcoal has sometimes a small deep red incrustation on it.

The estimation quantitatively of silver is effected in two ways. First, by the usual wet operations of the laboratory, and, secondly, by peculiar operations, termed assaying operations.

The chemical estimation of silver is always effected by precipitating the metal as chloride, and subsequently separating and weighing the latter. The solution containing the silver is first acidified by nitric acid, then a slight excess of hydrochloric acid, or sodic chloride added, after which the whole is boiled, to prevent any argentic chloride passing through the filter. Any considerable excess of either of these precipitants must be avoided, as argentic chloride is soluble to a small extent in either one.

It is next filtered, in a previously well dried and weighed filter. The supernatant fluid being first passed through, and the chloride then washed in with a little hot acidulated water (acidulated with nitric acid). It is then repeatedly washed, first with the same, then with pure water.

The filter is then dried again, with its contents, in a water-bath, until it ceases to lose weight, and, lastly, weighed carefully, the weight minus that of the filter will now be that of the chloride. This may be done without ignition, for there are two sources of error arising from ignition; first, some silver will very likely be reduced from the chloride by the carbonaceous matter of the filter; and, secondly, argentic chloride is itself volatile to some extent. Therefore the error is, perhaps, least in weighing the filter carefully before and after the filtration, having previously dried it perfectly each time, and used a filter as small as practicable, as above detailed. If, on the other hand, the chloride be fused, it is best to remove as much as possible to a porcelain crucible, and then burn the filter, subsequently igniting the whole, until incipient fusion, and weighing.

It is well also after adding the ash to the crucible, to put in a few drops of dilute nitric acid, and warm it up so as to convert any reduced metal into nitrate. A few drops of hydrochloric is then added, and next the crucible heated to dry all, and then to incipient fusion, before weighing.

If the quantity of chloride operated upon be large, it may be washed by decantation, the precipitation being effected in a flask or stoppered bottle, the fluid being heated in it to about 150° F.=65°·5 C., the precipitant is added, and the whole vigorously shaken, so as to break up the chloride; the clear fluid is then poured off, and washing effected by repeated quantities of distilled water, at first containing a little nitric acid, and at last with pure water. In effecting this, the chloride, after first settling, is to be transferred to a small crucible, and in the latter the washing above mentioned is performed; the vessel being gently heated before each decantation. When thoroughly washed, the chloride is to be dried very carefully, and subsequently heated, until the little cake just adheres together; and in this way it may be even handled with a pair of tongs, and weighed, the great thing in effecting this condensation being a few careful taps upon the bottom of the crucible at the removal of the last portions of washing water.

In analysing amalgams of silver and mercury, or separating them, the silver not being volatile, it suffices to heat to redness in a porcelain crucible; the mercury is then driven off, and estimated by the loss of weight found. But a more accurate method consists in making a solution of the metals, and then boiling it freely with a little nitric acid, so as to ensure the peroxidation of the mercury. Next add hydrochloric acid, until all the silver is thrown down; this, then separated, washed, and weighed, with the precautions already detailed, gives the amount of silver. If the mercury had not previously been completely peroxidized, some of it remaining as mercurous oxide would go down as calomel with the argentic chloride. In this operation enough hydrochloric acid must be used to ensure also the conversion of all the mercuric nitrate into chloride; for Wackenroder finds that argentic chloride is somewhat soluble in mercuric nitrate. Therefore to the solution (rather dilute) and acidulated with nitric acid the hydrochloric acid is added as long as any precipitate falls. This is allowed to deposit, and then filtered; next heated with a little nitric acid to free it from any basic mercurial salts. Water is then put on it and a few drops of hydrochloric acid. After which the argentic chloride is filtered and weighed. The mercury is then estimated by adding dihydric sulphide to the liquid filtered from the argentic chloride; this will precipitate the mercury as sulphide. Separate this, and mix it in a flask, with about an ounce of pure, slightly dilute hydrochloric acid. Now, on passing a stream of chlorine gas into this, mercuric chloride will be formed. This is separated from precipitated sulphur, boiled to expel the excess of chlorine, and then the mercury precipitated for weighing, by the addition of stannous chloride. See page 146.

As for commercial purposes the above analytical operations would be tedious, especially where many estimations of silver were required, a class of operations come into use, known as assaying.

In these the precious metal alone is separated, other constituents of the ore or alloy being disregarded. The details and practice of the operation differ widely according as to whether it is performed upon an ore or upon an alloy; but, in both cases, the concluding steps of the operation are the same, and resolve themselves into a cupellation of the metal for a final separation of the silver contained in the ore or alloy. Hence, in regard to ores, the first operation consists in forming an alloy of the silver with lead, this lead being furnished by a body used in the way of a flux, viz. by litharge.

Now, as it is best to have no more metal for the subsequent cupel operation than is absolutely necessary, the fluxing with litharge is an operation requiring much care, as the ore itself is apt to vary very much in its effect upon the litharge, and so render different and opposite modes of treatment necessary. For example, most ores contain sulphur, or other bodies, which have a strong affinity for oxygen; hence such would very readily reduce the litharge. Therefore, in order to prevent this taking place to too great an extent, it is found necessary to add also an oxidizing flux, as nitre, to counteract in sufficient degree the reducing power of the ore. Then, on the other hand, the ore may naturally be of an oxidizing character; in which case not only will no oxidizing flux be required, but, on the contrary, a reducing one, such as argol, must be used; while, lastly, the ore may chance to possess just the reducing power requisite to act sufficiently upon the litharge, and no more; in which case the litharge alone is employed.

From all this it will be seen that the first step required in the assay of a silver ore is one whereby we may learn its nature in the above respect. For this purpose Mitchell advises a preliminary assay upon about 20 grains of ore, which is to be powdered, and mixed intimately with 500 of litharge. This mixture is put into a small crucible, capable of containing about double the bulk; the crucible is heated very gently at first, but, after a time, the heat is to be quickly raised to a full red, so as to complete the operation as speedily as possible. When cool, the pot is broken, and the button removed and weighed. It may be that but little lead has been reduced, perhaps not more than half the weight of the ore used. In such a case an actual assay would be made of the following mixture: 200 grains of ore, 200 of sodic carbonate, 1000 of litharge, and 15 grains of argol, for the purpose of assisting the reduction of the lead. Secondly, If the trial button should weigh about double the weight of ore employed, then the same mixture would be used, except as regards the argol, which must be omitted, and about 50 grains of nitre used in its place. Thirdly, If the trial button weighed about the same as the ore, then litharge alone would be employed, without either reducing or oxidising flux.

The mixture being intimately made, as above, is to be put into a proper-sized crucible; and it may be here observed, that, in all cases where nitre is employed, either in assaying or melting operations, a very capacious crucible should be taken, as considerable action is always set up. The mixture is next covered with a layer of salt, and, lastly, with about 200 grains of powdered borax. The crucible is put into the furnace, and the gentle heat at first used, raised until the fluxes are well liquid; at which point the assay will generally be found completed. The pot is then removed and, when cool, broken, the button hammered so as to separate all the flux, and reserved for subsequent cupellation.

There is another operation, applicable in all cases, and especially in such as the estimation of precious metal, either gold or silver, in the sweep of the workshop, where portions of solder containing tin, as also considerable quantities of foreign matters, are associated with the metals to be estimated. It consists in heating the specimen under examination with a quantity of granulated lead in a shallow clay vessel, or scorifier, as here figured; this is so placed in a muffle (E, fig. p. 192) as that a current of atmospheric air may pass over the surface of the vessel and oxidise portions of the lead. This oxide of lead then forms a menstruum for the suspension of foreign matters, and

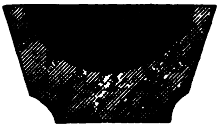


Fig. 41.

combines with silica as a fusible slag; while the portion kept unoxidized will retain the gold or silver sought for in the sample.

The operation is carried on as follows:—A quantity of about 50 grains of the sample is weighed and powdered; this will be about the quantity workable in one scorifier, but it is advisable to work this, as all assays, double: hence two scorifiers are prepared. A quantity of granulated lead is next taken, and the amount required may range from twelve to thirty times the weight of the ore or sweep. The quantity required will be large if much tin or zinc be present, or if (as in the case of an ore) it contain a large proportion of lime-salts. Half this amount of lead is first put into each scorifier, and upon it the 50 grains of the specimen previously mixed with 50 of borax. The whole is then mixed and covered with the remaining half of lead. The scorifiers are then placed in a heated muffle, and the opening closed up for a quarter of an hour, so as to fuse the lead. The heat is then allowed to fall, the door of the muffle opened as in carrying on a cupellation, and the roasting of the mass commenced. A slag will form first at the edges of the bath, and increase over the surface; but as the lead oxidizes it becomes quite fluid. The whole should be now occasionally stirred, so as to keep all parts mixed. The heat is then raised, whereby the whole is rendered liquid. This may be judged of by the facility with which it runs off an iron stirrer which is crooked at the end so as conveniently to be dipped into the bath. Thus, under the influence of the borax, the metallic particles are so cleansed, as to run well together, the borax assisting also in the formation of a liquid slag from the first. The assay being in this limpid state at the end of the operation (which will be completed at the end of half-an-hour to three-quarters), the scorifier is removed, and its contents poured quickly into an hemispherical iron ingot mould. Thus a button is obtained, consisting of a greenish slag at the top, covering a button of metal; these are to be separated by a blow of the hammer, and the metal again reserved for cupellation, and parting for gold.

If the operation has been well performed, this button will be tolerably malleable, and the slag quite free from any beads of metal.

If these be not so, the assay is not trustworthy. The working may be divided into three stages, namely, of about a quarter of an hour for the first fusion; next, twenty minutes for the roasting and oxidation; and lastly, ten minutes for the final fusion of the whole.

The operation of cupellation, or, as it is often called, the dry method of assaying, is applicable to all alloys of silver, as coin, &c. It is a process of great antiquity and beauty, and takes its name from the little vessel, or cupel, wherein it is performed. It is based upon the property which characterises the precious metals, viz., that when heated to fusion, and exposed to a current of air, not the least oxidation takes place, while such treatment of base metals constituting alloy, under certain conditions, perfectly oxidizes them. So that, by this means alone, we are able to get rid of the alloy associated with a precious metal.

These cupels are small blocks of bone-ash, with a concavity, or cup, formed upon the upper surface. For their manufacture, bones, which consist of a mixture of animal and earthy matter, are burned. In this way the former is decomposed and separated; the latter, consisting chiefly of calcic phosphate, mixed with a small portion of calcic carbonate, remains. This is well washed and dried.

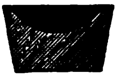


Fig. 42.

The cupels are made by moistening a quantity of this ash with water just to dampness. The best method of effecting this consists in heaping up some five or six pounds of ash in a small tub or tray; a hole is then made in the centre, at the top of the heap, just large enough to contain sufficient water, which is poured into it, and the hole then covered up with ash. The whole is allowed to stand for 12 to 18 hours, when the ash will have absorbed all, and become in just a fit state for working, appearing as a damp powder. Into a steel mould (1), having a taper hole turned in it of the external diameter of the cupel, a quantity of this moist ash is pressed. A collar of gun-metal (2) is then placed round the mould, in which a former (3),

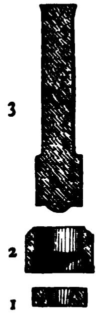


Fig. 43.

also made of steel, and having a well-polished convex end, is put. Both the mould and former should be of well-hardened steel. The stamp or former is then struck two or three blows with a hammer of some 5 lbs. weight. The mould is then separated again, and the cupel knocked out by a gentle tap on its under side.* A well-made cupel should be perfectly smooth in the basin; for it, the ash employed should not be too fine, or the absorption is not good, and the assays are apt to stick very tightly to it; while it should not, on the other hand, be too coarse, or there will be loss of the metal. Then the cupel, when well dried, should not crack on heating, especially in the basin; but if the method for making them here detailed be followed, such cupels will dry quite solid, although porous in texture; and when seasoned will heat without cracking in the least. The term seasoned is used, as it is better if possible to keep cupels at least three or four months before using them.

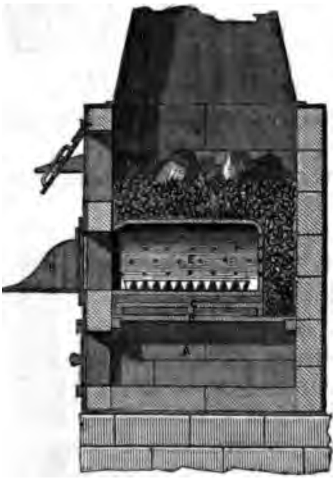


Fig. 44.

In these cupels the silver is fused with a quantity of lead, and in a furnace of a construction which admits of free circulation of air above the heated cupels, with (at the same time) the most complete arrangements for regulating these oxidizing currents, as to quantity, intensity, and direction. Such a furnace is called a cupel or muffle furnace, from the chamber in which the former are placed in working.

It is best formed in stout wrought-iron, lined with firebrick. It is oblong, with the long diameter from back to front, and may be built internally as large as about 13 inches wide, by 1 foot 5 from back to front, and 2 feet 7 high. At the lower part is formed an ash-pit, A, which with its brick bottom occupies 9 inches of the height. Next an inch is taken up by the fire-bars, B, which are of that depth, and formed with shoulders which rest on bearing bars placed back and front: these shoulders are flatted out, so as to keep the bars ½ inch apart at their top sides for air spaces. Upon these bars, and standing on inch legs, is placed a plate of iron, C, ½ inch thick and 13 inches long by 8 wide; next upon this is a bed of fire-clay, of ½ inch in thickness, and by the latter the muffle itself is fixed to the iron muffle-plate, so as to form a compact mass. The floor of a full-sized muffle, E, is just of the dimensions of the plate above described, and it is 7 inches high. Then above the muffle is a clear space, F, of 1 foot in height, and this, with the spaces left round the muffle arrangement, down to the bars, form the fire-chamber. Thus it will be seen that the muffle-floor is heated by conduction through the mass of material, for the fuel should not be at all under the muffle, but only at its sides and above it.

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* They are, at times, made by a screw press, but a good hand-made cupel is to be preferred, especially for silver.

The front of the furnace should be provided with five openings, arranged thus:—One in front of the ash-pit closed by two sliding doors, A, whereby the draught may be controlled. Next one on each side of the muffle and at the ends of the fire-bars, B B; these are made only just of a size to withdraw a bar on each side, and so admit of the fuel being dropped down into the ash-pit. Thirdly, a door, C, of the shape and size exactly corresponding to the neck of the muffle; this should slide down in grooves on the side, and

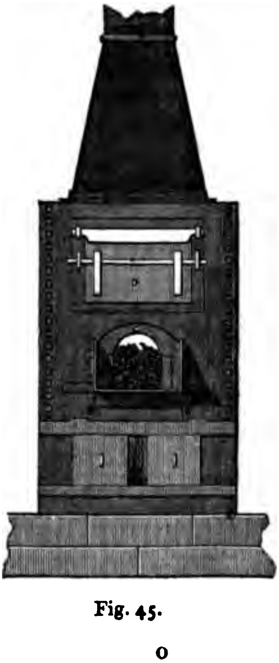


Fig. 45.

should also fit as tightly as possible, being notwithstanding very free to slide up and down. And in order to ensure its closing quickly and perfectly the iron should be nearly if not quite a quarter of an inch thick, the face of the furnace mouth also being strengthened with similar thick metal, in order to prevent its twisting and so preventing quick and close shutting up.

In front of this muffle-door is built out a gallery (H, fig. 44); this serves to contain the mouth coal hereafter spoken of as employed during the working of the assays.

Lastly, an opening, D, is formed above the muffle for feeding the furnace, and the door for this is provided with a bar to latch it to, while by sliding upon an inclined wedge-shaped ear on each side, as shown in fig. 44, it admits of air entering; and so by this we are capable of much modifying the draught of the furnace. The whole arrangement is surmounted by a taper hood, which terminates in a chimney; this hood also having a damper in it, which when put in will close the opening to the chimney completely. The furnaces erected by Mr. Field, lately the Queen's assayer at the Mint, are of this description.

The metal employed for constructing them should be good charcoal plate of about one-eighth of an inch thick, and the sides, back, and front, riveted to 'angle-iron' placed on the inside at each angle.

It will doubtless be seen at once, that by means of the ash-pit, muffle, and feeding-doors, together with this damper, a most perfect control of the fire is obtainable; both as to its temperature, and also the capability of giving any course desired for the ingoing current of air to the burning fuel.

The muffle itself is a kind of oven formed of fire-clay. Its size should be well proportioned to the furnace in which it is set, although circumstances of position of the furnace-room, height of chimney, &c. &c., will very much modify the proportions of muffle-furnaces. In the author's own laboratory he was compelled to put up three sets of furnaces before arriving at proportions most suited to perfect working; thus it will be seen that no definite sizes can be given which will be universally applicable. But a muffle for the furnace described may measure 13½ inches long by 7 high and 8 wide. Its sides should be bored with a number of holes from the outside, having a direction from below upwards: thus, although they freely give passage to currents of air outwards, their direction prevents the passage of small cinders inwards. These holes are much preferable to slits (as formerly made), and should be carefully placed, in regard to the position of the cupels, so that a current passing over particular cupels should be at once carried directly out into the fire; and there should be a row in the end of the muffle at the top, which will tend to clear the muffle of fumes: for it must be stated that during the working of assays no traces of fumes should be visible, but a perfectly clear atmosphere exist inside the muffle from beginning to end of the operation.

The old slit muffle was very objectionable, and good results, in silver work especially, hardly to be obtained in it, for the spaces being necessarily large cause very unequal currents, and again, after such a muffle has been heated, it is almost certain to crack from one or more of the slits, and often quite across the roof of the muffle itself. Then their size admits of the falling in of the carbonaceous matters of the fire. These evils caused the author with Mr. Field to institute a number of experiments more especially upon silver fires, employing muffles perforated as described, instead of with slits, and the result of these was the construction of a muffle wherein the draught is carried uniformly over the rows of cupels, by means of a series of holes carefully placed, and sufficient in number. This muffle is now made and sold by the Plumbago Crucible Company as the 'Mint Muffle.'

In fitting up these muffles in the furnace, the plate, being first carefully fitted in its place, is to have the clay bed (well kneaded) put upon it; next the muffle firmly pressed on, and on the top of this latter a good coating of fire-lute, which assists in retaining heat, and also protects the muffle from blows of coal, &c. A slow fire is then put into the furnace, and the muffle-fitting dried quickly, so as to crack it well; these cracks being subsequently mended, the whole arrangement will be as a solid mass.

The furnace just described is a full-sized one, and is adapted to work forty-five or fifty silver or gold assays at one operation; but equally good results may be obtained in very much smaller furnaces, down even to a muffle so small as to work only six similar cupels at one time.

The fuel suited (beyond all comparison) for assaying operations is charcoal; but the large consumption of a full-sized furnace, and consequent great expense, together with the necessity for increasing largely the capacity of the fire-chamber, have caused other fuels to be adopted in its place, and thus anthracite coal and coke are much used. If the former be employed, we must be careful to obtain the best varieties only. By its use we can command a great body of heat in a small space, while, from its density, its combustion is comparatively slow. The fire requires lighting by arranging the furnace, first with some quick-kindling wood, then a small layer of charcoal, and lastly with anthracite coal. Where charcoal alone is used, the old practice was to fill the furnace, and then on the top to throw some lighted fuel: thus the fire burns downwards, and the whole apparatus is gradually heated up; but a furnace will, by such working, require from two to three hours to get in working condition; while with anthracite, as above described, it will be well hot in from an hour, or even less, up to an hour and a half.

Mr. Charles Griffin has adapted an oval body (*a*) to his gas melting furnace (fig. 11), which thus admits of the insertion of a muffle for cupellation, with gas as a fuel. The muffle is placed so that the floor of it is from 1½ to 2 inches above the top of the burner: thus a good body of flame is made to envelope it; and by a plate of fire-clay being placed across the furnace, just above the muffle, the flame is turned down and passes lengthways upon the crown of the muffle towards the chimney. It is large enough to work 12 to 15 cupels at an operation, its internal dimensions being 8 inches long by 4 wide

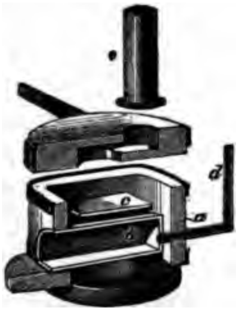


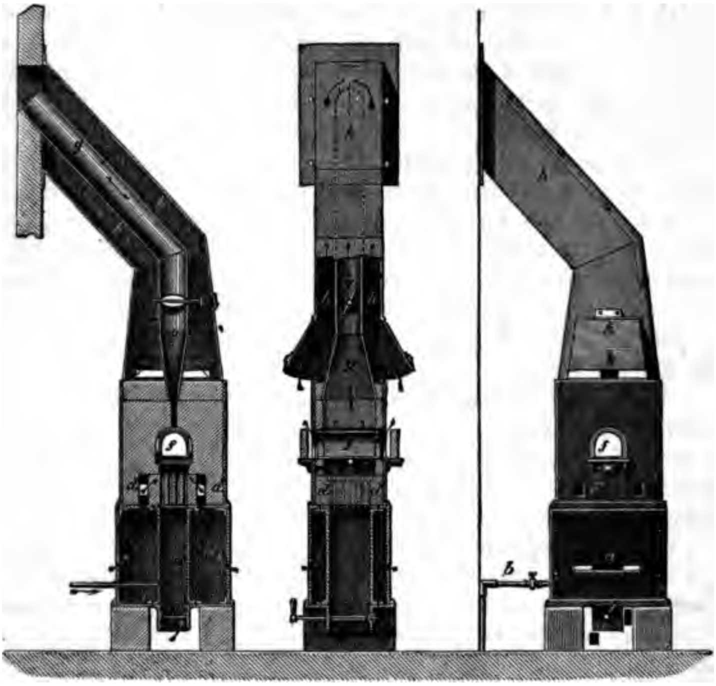
Fig. 46.

and 3½ high. In his earlier furnaces the muffles were somewhat smaller, and formed with a few longitudinal slits on the crown at the back; but in muffles of the dimensions given an outlet tube (*d*) is formed in them at the back, which passes out through the furnace wall; and to this a small sheet-iron chimney is attached, of about 3 feet long by 1 inch diameter; in this a small valve is formed, by means of which the draft can be diminished if needful. In other respects the arrangement of this furnace is the same as that of the melting furnace before mentioned, excepting only that for the larger muffle a somewhat longer chimney (*e*) is needed: hence an extra 2-feet length is added.

With good management this furnace is very effective, and gives excellent results. Then, besides the advantage of working without solid fuel, we have the great one of getting the heat up in about twenty minutes to half an hour from the time of lighting, and, again, great power of draft regulation, as well as of slowly cooling down at pleasure,—indeed, all the requirements of an ordinary assaying furnace. The consumption of gas is from 30 to 35 feet per hour.

Mr. Arnold J. Watson, of the Assay Office, Sheffield, has devised a gas assay furnace, which he has had in operation at the above office since March, 1867, and he states that it has given entire satisfaction. One great peculiarity in it is, that the muffle, which is of large dimensions, viz. 5½ inches broad by 12 long upon its floor, is yet open at both ends. Mr. Watson makes from 24 to 32 assays at an operation, and upon silver,—a trying test of the working powers of a muffle furnace. He says, in his furnace 'ordinary coal-gas, mixed with atmospheric air, is employed as a substitute for charcoal, anthracite, or other fuel now commonly used.' It is represented in figs. 47, 48, and 49.

The apparatus consists of a cast-iron cylinder (*a*), in which the gas and air are mixed, and to which are fitted a pipe (*b*), with tap attached, for the admission of gas, and a valve (*c*), worked by the handle (*c′*), for regulating the proportion of air required for the combustion of the gas employed. Upon leaving the cylinder (*a*), the gas and air, in a mixed state, pass through the perforated fire-stone burner (*d*) into the lighting chamber (*e*) underneath the muffle (*f*). In this chamber the mixture is ignited, through the opening (*e*″), which is afterwards closed by a fire-stone plug (*e*‴); and the flame, rising from the surface of the burner, entirely envelopes the muffle, passing away through the chimney (*g*). The draught, besides carrying away the products of combustion, converts each jet of gas, as it issues from the fire-stone burner, into a 'blowpipe flame.' This is in a measure effected by currents of air which are drawn through grooves cut on the surface of the burner, between each series of jets. These grooves, being invisi-



Figs. 47, 48, and 49.

ble in any of the views given, are merely dotted in, to show their position. The flame is smokeless, and of a blue colour, producing a sufficient heat for assaying purposes within one hour after lighting.

The heated chimney creates a current of air inside the casement (*h*), by means of which the oxide of lead, or any vapours proceeding from the mouths of the muffle, are conveyed away, a hole being made into the flue above the furnace-chimney, and within the casing, for the purpose of allowing them to escape. The improvement in the muffle consists in its being open at both ends: by this arrangement the assayer is enabled to watch the progress of the assays, and to regulate their working more effectually than is possible with the ordinary muffle.

The fire tools required for the ordinary anthracite furnace are shown in the drawing, fig. 50; they are,—

1. A stirring-down tool, for arranging and compacting uniformly the fuel round the muffle; it is used at the feed-door, D, fig. 45: by this operation the fire is freed from hollow places, which would create unequal draughts in the various parts of the muffle.

2. A strong shovel, with holes, so as to charge in the coal free from dust.

3. A teaser, for raking out the fire-bars, so as to draw up any particular portion of the fire in which, by obstructed draught, it may burn dull and sluggishly.

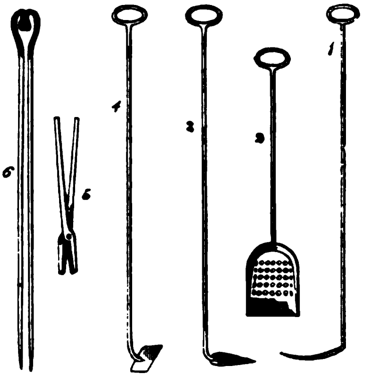


Fig. 50.

4. A fire-hoe, for withdrawing ash from the ash-pit. This should be cared for before charging in the assays, and after stirring down and clearing the fire-bars. This tool is also employed to scrape and clean the muffle-floor.

5. A small pair of strong tongs, for removing and replacing the iron muffle-doors and others.

6. Charging-in tongs, for putting the assay and lead into the cupels. These require to be most carefully made: they should be of good, half-round steel rod, and worked tapering to the points by forging, the points coming well opposite each other; and the object of using good steel is that they shall maintain their form and qualities, which iron would lose by fire use. Two pairs are needed—one of about 3 feet long, for the back of the muffle, and the other about 2 ft. 2, for the front. The back bend should be heavy enough to balance the legs, when held, as they are, by the hand comparatively near to this bend.

Now the practice of assaying silver by cupellation resolves itself into the following operations. First, the very accurate weighing of a certain fixed quantity of the specimen to be operated upon; secondly, the cupelling this with a proper quantity of pure lead; and, thirdly, the re-weighing the button of pure silver so obtained, when the loss of weight will be due to the alloy separated. This accurate weighing involves the use of a balance of the most delicate description. The one employed by the author is an instrument of his own construction, and described by him in the 6th volume of the *Quarterly Journal of the Chemical Society*, page 36. Its essential parts are represented roughly to scale in fig. 51, and again as enclosed for use in fig. 52. It consists of a very light skeleton beam, 10 inches long, $\frac{1}{2}$ inch deep at the fulcrum, and tapering off to $\frac{1}{3}$ inch at each end; it is about $\frac{1}{16}$ inch thick at the centre, decreasing in the same way to $\frac{1}{20}$. As little metal as possible is left in it; thus, in the centre there is but just enough to allow of secure fixing for the knife-edge; and at the ends, for adjustment of the length of arm, &c. This latter is effected by the ends being loose, and adjustable by screws, which fix them at the accurate distance.

The bearings for the pan pendants are two hard steel points at each end, adjustable (so as to bring the two end and centre bearings in a straight line) by having a fine screw cut upon each, and provided with fixing-nuts. By these the points can be screwed up or down, through the horizontal plate formed at the end of the beam.

The pendants are hung on these points by a small steel plate, in the underside of which a cup-shaped cavity is turned for the front, and a groove for the back ones.

The knife-edge in the centre rests upon agate bearings, which latter, instead of being plain, are worked to elliptical faces, the axis of the ellipsis being parallel with the beam; hence the knife-edge bears virtually upon points.

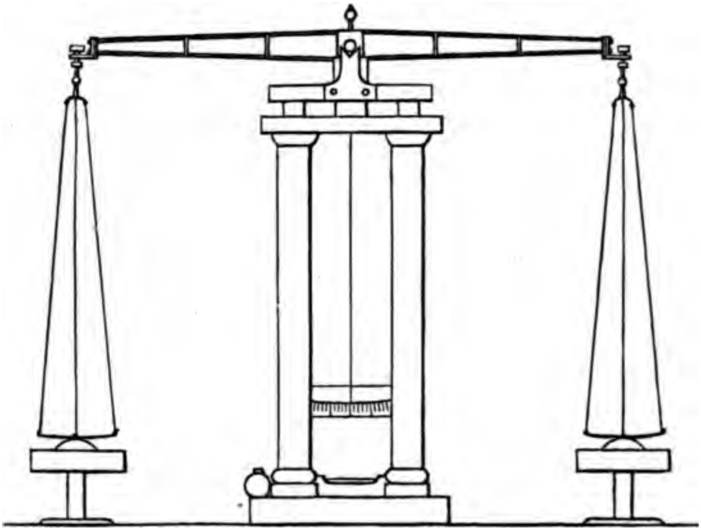


Fig. 51.

Bearing in mind the very small weights these balances are intended to carry (which should not exceed 25 to 30 grains), no hesitation existed as to reducing all parts of contact where friction during action occurs to the smallest possible dimensions; and indeed, although the author had used two of these instruments in daily hard work for nearly ten years, at the time of first printing their description these delicate parts showed no indication of wear by any diminished sensibility. The stand is massive in its construction, in order that when put into action, no tremulousness may be communicated to the beam; it is formed of two stout pillars of ½ inch diameter, and 6¾ inches long, fixed on a base ¼ inch thick; upon the upper end of these is fixed a table, which has two upright pieces rising from it, to which are cemented the agate bearings. A second corresponding table is attached to the movement-rods which pass down the pillars. This table has two mortices in it, for the passage of the upright pieces which carry the agates, and upon these uprights as guides it slides up and down. On the outside of this second table is a crutch on each side; these lift the beam slightly off its bearings, when throwing it out of action.

The movement-lever on being depressed, first, however, acts upon the arms of two rollers, which are fixed under the lanthorn, and whose opposite arms depress the ivory tables which support the pans. By the time the tables are well away from them, the lever has reached a connecting stirrup between the movement-rods, and begins to drop the beam upon the agates.

The tables have a small hemisphere of agate fitted in their centres, and the pans themselves have a curve given them of a radius just equal to the distance between the ivory table and point of suspension; by these provisions, should they swing out of the perpendicular, during weighing, they will nevertheless be caught at any point by the tables when they rise up to them.

By the pillars being fixed at a distance of 1½ inch from each other, a good space is obtained for the scale; while by prolonging the index-needle to rather more than 6 inches downwards, very open degrees are obtained. And besides this great advantage, the motions of the index-needle are brought nearly upon a level with the pans, and thus altogether under the eye.

An instrument thus delicate is absolutely necessary, because the smaller the quantity of metal we operate upon (within certain limits), the more successful will be the operation; and although we could, by using a heavier instrument, get nearly as close weighings, their performance would be very slowly effected, and with less certainty. The author sent the drawing for this balance to Mr. Oertling for its construction, with the direction to him to get the beam as light as the frame could be worked (in brass), and in the first instrument made it weighs 122 grains. Subsequently upon the balance coming into considerable use in foreign mints, one was ordered for our own Mint, and the author under-

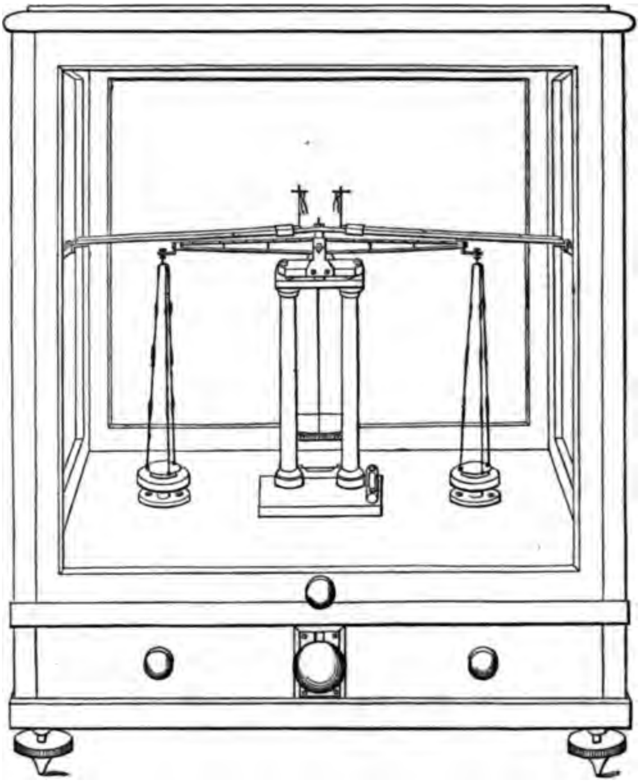


Fig. 52.

took to see that as delicate an instrument as could be made, should be supplied to them. The beam of this was brought down to 84 grains. He then had one made for his own use in aluminium, and to this Mr. Oertling applied small ruby points in place of the steel ones. But although the specific gravity of the metal used was so low, the beam yet weighed 78 grains from the impossibility of working aluminium to so delicate a frame as brass could be reduced. These points have been thus dwelt upon, as the speed and constancy in a beam depend upon the small mass put in motion, the centre of gravity also being adjusted so as to be just below the fulcrum.

The quantity taken for examination is called an assay pound, because it is a representative of the troy pound: hence, in silver work it is subdivided in the same way, viz. into ounces and pennyweights, the halfpennyweight being the smallest denomination to which, in Great Britain, silver assays are reported, although an assayer with such a balance as the above can weigh accurately to half a troy grain, even with a small assay pound.

This assay pound may be any quantity, chosen according to the particular views and practice of the assayer, and may range between 6 and 12 grains: the quantity generally used by the French assayers is the gramme, or 15·434 troy grains, but for several reasons this is too large for cupel assays, and less calculated to give correct results than a smaller quantity. A ten-grain pound is a very good one for silver. The old assayers always worked with ounce and pennyweight divisions of this, but a better plan is to work decimally, and, if trade estimations be required, to convert the decimal into the trade expression.

Decimally then, fine silver would be called 1000, and English standard silver, which contains in the pound troy, 11 ounces and 2 dwts. of silver, mixed with 18 dwts. of alloy, would be ·925. Mexican dollars are a mixture of 10 oz. 16½ dwts. of silver, with 1 oz. 3½ dwts. of alloy. Hence, as all the excess of alloy over the English standard would be called 'worseness,' they would be reported worse 5½ dwts. The decimal weighing of such an assay, if truly made to the Mexican standard, would be 902·7; actually worse 5 dwts. 8 grains: but as trade reports are only made to each ½ dwt., it would be reported W 5½ dwts.

To take one other example, the French standard contains 900 parts of silver with 100 of alloy: now this is exactly equal to 10 oz. 16 dwts. of silver with 1 oz. 4 dwts. of alloy. Hence this would exactly be, worse 6 dwts.

On the other hand, certain Indian rupees contain 950 parts of silver with 50 of alloy: this would be equal to 11 oz. 8 dwts. of silver with 12 dwts. of alloy. Hence the trade report for these would be, better 6 dwts.

The first step, then, in the assay of a specimen of alloyed silver, is the careful weighing of an assay pound of the sample: for this purpose the cut from the bar is flattened out to a thin disk; off this the edges are carefully cut, and from the centre two assay pounds are prepared by an assistant, in a less delicate balance than the one described; as being more quick in action for rough weighings. The assayer himself then verifies and corrects these rough weighings in the fine balance, and proceeds to wrap the metal up in a piece of sheet-lead, amounting in weight to just half the quantity required for cupellation. This varies much, increasing just as the amount of alloy in the specimen increases. Most writers upon this subject have transcribed a table by D'Arcet, wherein he commences with fine silver, and states that it requires $\frac{3}{10}$ of its weight of lead for cupellation; that English standard may be cupelled with five times its own weight, increasing the quantity of lead as the alloy increases, until the latter amounts to 500 parts of the thousand. To such a silver he would give 16 to 17 times its weight of lead, and no greater quantity to any coarser specimen.

But from the author's experience there are great difficulties in working, even fine silver, with less than three times its weight of lead; nor does he believe that results obtained on the finer qualities of silver are worthy of trust with a less quantity. English standard will require six times its weight, and coarser varieties in like proportion.

The estimation of the quantity of lead required will be a matter for the experience of the assayer. A practised operator will judge very closely by the hardness or softness of the cut of the metal, joined to its colour, and the like, and seldom be far out; but when there is any doubt upon this point, it is better to err on the side of too much rather than too little lead. The French works on assaying recommend the use of a paper case for the metal, but this is a most clumsy expedient; and if this, with other details of the operation contained in such sources, be the usual French practice, it is not surprising that some other method of silver assaying should have been found needful in France, as also in other places where their little fire-clay assay furnaces are used, and with such methods of manipulation also as are employed in working them.

It is almost needless to remark that lead, as free as possible from silver, must be employed; and on any purchase of fresh lead the amount of silver contained must be tested. Still, as the proofs assayed with the whole set are done with the same lead, the importance of this is, to some extent, diminished.

The specimens are then carefully wrapped in their lead cases, these cases weighing, as before stated, about half the weight of that required. If many are operated on at once, they are carefully ranged in distinct compartments of a mahogany tray: this latter is well to be made of the size of the muffle-floor, with compartments corresponding to each cupel. While these weighing operations are going on, the fireman having lighted the furnace and put the requisite cupels in the muffle, the heat is gradually got up, and examined from time to time. When the muffle is of a uniform bright red and the cupels have lost all ashy appearance, the fire is 'stirred down' by the assayer. This is done by putting in a stirrer (No. 1, fig. 50), at the top or feeding door, and with a light hand, pressing the fuel all round the muffle, so as to prevent or rather to fill up cavities in it, which would otherwise cause draughts through the muffle towards them, instead of allowing the current to flow equably over the whole muffle floor as it does when the fire is thus nicely compacted. The furnace is now opened; and in the muffle-door is built up a series of pieces of

charcoal, commencing with some large pieces, then following with a layer of smaller, and so on, until the mouth is about two-thirds built up, as seen in the front view of the furnace. An assistant then puts the remaining half quantity of lead into the cupels; when this is fused the assayer carefully charges in the assays, and when all are in, completes the mouth with small twigs of charcoal. The working, or oxidation of the bath, is then started, by first throwing a current of air through the muffle. This is shown by the bath of metal becoming covered with small patches of oxide of lead; these circulate from the centre over the edges. The working thus fairly set up, the adjustment of draught by means of the various furnace openings is to be made, so as to maintain a steady circulation from the centre to the circumference, where the oxides appear to be absorbed by the cupel. During this working, no appearance of fumes should be manifest; indeed, nearly the whole of the oxides should pass into the cupel, and that they do so in a well-executed assay may be proved by weighing the cupel before and after the operation, when it will be found to have gained very nearly the weight of lead used plus its proportional of oxygen.

In two experiments cupelling 92 grains of lead at each operation, No. 1 gave 97 grains and No. 2, 94 grains of lead oxide absorbed. The calculated quantity would be 99 grains.

The globule of fused metals goes on diminishing in size, until, after from twenty to forty minutes, the whole of the lead and base metals will have been oxidized. Just as this occurs the globule suddenly displays a most brilliant appearance, dependent upon the red-hot mass of silver being visible through a thin film of oxide of lead: this appearance is termed the brightening of the assay, and is immediately followed by an exquisite play of prismatic colours over the button; these flutter upon the surface for a few seconds, and then clear off, leaving a bead of pure silver. The appearances during the whole operation are most beautiful, and hence no other metallurgic operation upon the small scale can compare with this. But in cupellation on large bulks in the refinery they are altogether absent, and Percy, in his description of the latter, justly remarks upon the glowing descriptions given by some authors of really imaginary appearances.

If the furnace management be good, the 'going off' of the assays will commence with the row in front, and pass back from row to row to the last. If, on the other hand, the working off occurs irregularly, and at all parts of the muffle, perhaps coming even forwards from back to front, it is an indication of bad fire-work, and the resulting assays will turn out very unsatisfactory. The arrangement of 'mouth coals,' as the charcoal in the muffle-mouth is termed, is very advantageous, tending much to regular working. It soon takes fire at the inner end, and by its slow, steady combustion keeps up the heat of the assays near to the external cold current of air, which latter is thus warmed on entering; and, moreover, the too violent oxidizing agency of common air is diluted by an admixture of carbonic anhydride. Then, again, the regular working of all parts of the fire may be insured by removing some twigs where necessary, or inserting others where the working is proceeding too rapidly. And from these remarks it will be seen, that from the time of charging in until all are worked off the furnace must be carefully watched by the assayer, or by a practised fireman.

It now remains only to draw out the mouth coals with a fire-hoe, which must be done quickly and completely, and the muffle-door dropped in, also quickly, the object being to shut all up without any sudden rush in of cold air, which would cause the assays to 'spring.' The whole of the furnace-openings are then closed up, and all allowed to cool down thoroughly, — a stage occupying from half to three-quarters of an hour.

The furnace is then opened, and the assays taken out into an iron tray. If they are good, the buttons will appear nicely rounded, the top slightly pitted, and their surfaces somewhat matted or crystalline, and they should adhere but slightly to the cupel. If the adhesion be much, and they throw out any projecting portions at their bases, they are not fine; and if, in place of standing up nicely rounded from the cupel, they exhibit a flat appearance, it is a sign that they have not had lead enough added to them. They are next separated from the cupel, just tapped with a hammer to knock off any adherent ash; for which purpose, also, they are subsequently carefully brushed with a wire brush. Tookey dips them in dilute hydrochloric acid, in preference to brushing them, for the removal of any adherent bone-ash.

Now the rationale of the operation is this:—When lead is heated in a current of air, it is readily oxidized, forming a very fusible oxide; this also is very ready to give up part of its oxygen to certain other metals: thus copper becomes oxidized, and its oxide, dissolved in the fluid litharge, passes with it into the texture of the porous cupel in which the assay is made.

It now only remains to weigh the assays and compare them with some well-known standards of comparison, worked in the same fire with the unknown alloys. It will be found that there is uniformly a loss, dependent partly upon silver volatilized and partly upon absorption by the cupel; and I believe that, in the latter, a small proportion of silver passes into it as argentic oxide. The loss is a fluctuating quantity, varying with circumstances, and especially with the temperature of the furnace: hence the standards or proofs used in the operation afford the best means of verifying the assays; and from a great number of these it may also be learned pretty closely what this loss should be, as a normal quantity.

For a considerable period of the early part of my own practice I was in the habit of employing nine standard pieces in a fire of fifty cupels, until, by experience of pretty constant loss in the same parts of the fire, their number could be reduced to five.

From the dry we may pass to the humid assay of silver,—an operation which had its rise in France, being contrived by Gay-Lussac in consequence of the uncertain results obtained in the French Mint by cupellation. It is performed by precipitating the silver after we have converted a known weight into nitrate, by sodic chloride; and then, having ascertained the quantity of the latter needed to effect this, we learn the quantity of argentic chloride formed, and, by consequence, the quantity of silver present in the specimen assayed.

This is a natural sequence of the law of combination in atomic proportions, for 108 parts of silver combine with 35·5 of chlorine in forming argentic chloride, and 35·5 is the atomic proportion of chlorine, whether it combine with silver, sodium, or any other body. Thus our knowledge of the quantity of silver sought is certain, when we know the amount of sodic chloride used for its complete precipitation. Suppose, then, an assay formed of fine silver be taken of 10 grains weight, and it is required to know how much sodic chloride will exactly precipitate this; it is a simple question of proportion, thus stated:—As 108 (the proportional of silver) is to 60 (the proportional of sodic chloride), so will 10 grains be to the quantity required, which will be found to be 5·555 grains. Having arrived at this quantity, a solution of salt is made, in the proportion of 5·555 grains to every 1000 grains of water: hence, 100 grains of this would completely precipitate 1 grain of silver; 10 grains, ·1 of silver; and so on. A solution so made, however, always requires correction after testing it with an assay pound of pure silver, for the calculated quantity of salt is generally found insufficient, as it is not easy to obtain quite pure sodic chloride; although, indeed, that is not absolutely necessary, as good ordinary common salt is very uniform in composition, and answers the purpose perfectly well. Several other precipitants have been used by different operators; but there is none, on the whole, to be preferred to common salt, which possesses many and great advantages.

If, then, it were desired to estimate the proportion of silver in a coin (an English silver coin, for example), the following proceeding would effect this:—An assay upon 10 grains, the quantity chosen, should be dissolved in a small quantity of acid by a gentle heat, the solution being made in a bottle capable of well stoppering. Next, some of the salt solution might be put into an alkalimeter, of a convenient form for weighing, and the instrument and its contents very accurately weighed. A quantity of the solution would next be added to the silver solution, until it was supposed something very near to complete precipitation was effected. Then, on stoppering the bottle and giving it a vigorous shaking, the chloride formed would agglomerate, and the liquid become quite clear. Salt solution is then to be added, a few drops at a time, shaking and clearing after each addition, until exact neutrality is attained. Lastly, by returning the alkalimeter to the balance and ascertaining the quantity of solution used, the amount of silver would be ascertained.

But the difficulties attendant upon such a method will no doubt at once be apparent, the chief of which will be seen to be the extreme care and expenditure of time necessary in order to arrive at the point of saturation, enhanced by the fact that errors of one or two hundredths of a grain in the silver estimate are considered grave ones, and may be produced by corresponding errors of one to two grains of solution too much or too little.

It might be imagined that if, in place of weighing, we used some means of measuring the salt, it would answer all purposes; but this is impracticable with a strong solution from the yet increased difficulty of measuring such small amounts in any ordinary way: hence, out of these difficulties the method now usually pursued arose, and which in outline is the following.

A solution of salt is made just as already described, and of this one constant measure is used in all cases,—1000 grains, for instance: hence, to accommodate this constant quantity, a varying one of the silver specimen is taken; such quantity of silver being regulated by presupposed quality of the alloy, and being just the amount which would contain our assay pound, or 10 grains, of pure silver, the excess of weight being due entirely to alloy.

An example or two, after description of the solutions and apparatus, will, perhaps, make the system plain.

First as to solutions.—For the preparation of the first, or 'normal solution,' some good clean salt may be procured, rubbed to powder, and well dried. When perfectly dry, a quantity may be taken—say for 100 assays; which would be 5·555 grains × 100 = 555·5 grains: this is next to be dissolved in 100 quantities of 1000 grains each = 14 lbs. 2 oz. 50 grs. of water. Then from this, after verifying and correcting its strength, a second or 'decimal solution,' is made, which, as its name implies, shall be just one-tenth the strength of the normal. For, as close indications are arrived at in an assay, concentration of the former solution being so great would require extremely small and accurate measurements; hence we employ this tenth solution, formed by adding 1000 grains of normal to 9000 of distilled water, and by so doing are enabled to make our fine additions of 10 grains measure instead of one grain only.

A third, or supplementary solution, is made of one assay pound (amounting therefore to 10 grains) of silver, dissolved in a small quantity of nitric acid, and then made up in quantity to 10·000 grains. This is called the 'nitrate-of-silver solution,' and it will be seen that, bulk for bulk, it will exactly neutralise the decimal salt solution. Its use will presently be seen.

Where many humid assays of silver are made, it is convenient to have the normal solution of salt kept in a large glass vessel (and a large German-glass Woulfe's bottle makes a very convenient receiver). Into one neck of this is to be inserted a syphon-shaped tube, of tolerably large capacity, so that at its lower end a small thermometer can be inserted; just below this the tube is contracted, so as to enter and cement into the upper end of a silver cock of peculiar construction; to the lower limb of this cock a pipette, of 1000 grains capacity, is cemented; supposing that bulk has been adopted as our normal

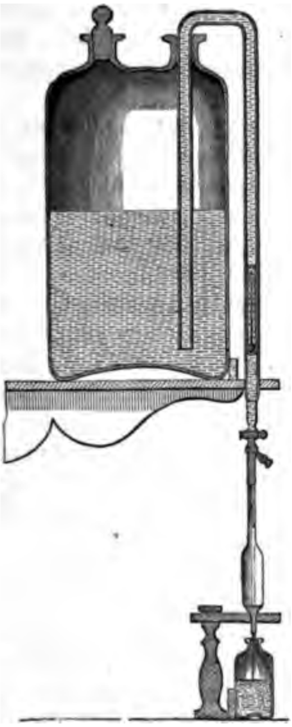


Fig. 53.

measure, but 100 cubic centimeters, or any other bulk chosen, may be used.

The whole apparatus must be so placed and proportioned, that the line on the stem of the pipette marking the 1000-grain point should be at about the level of the eye of an operator. The pipette line should be adjutsed just at the point from which it will deliver 1000 grains, leaving the drop in the point, which will be retained by capillary attraction, as an overplus not to be used.

The use of the thermometer is to ascertain the temperature of the solution as it flows over it; for as, of course, expansion by heat will by just its amount weaken the solution, so a correction is necessary for the temperature at which the assays are made. This, however, need hardly be mentioned as necessary, as no one would work assays without also simultaneously working a standard one for correction.

The cock, fig. 54, consists of a barrel and plug, as in any ordinary one, but the way through it from the plug outwards is continued by a small central tube, A. A small conical valve, B, enters the side of the main tube of the cock, just below the commencement of the inner tube; this valve being closed by a similarly shaped plug, which jams up on turning it, being forced up by a small screw-head, which works in a spiral slit in the side of the valve. This is for the admission of air into the upper part of the pipette, so as first to adjust the contents, and subsequently to cause their flow out.

The whole of the above apparatus is for the normal solution only. Then the decimal solutions of salt and of silver are best kept in wide-mouth stoppered bottles, from which they are measured out for use. For measuring these, a few small, straight pipettes are employed, graduated in five 10-grain divisions; or, in other words, with five spaces, each equalling one hundredth of the large

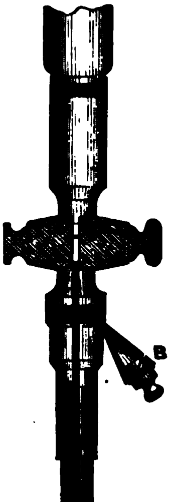


Fig. 54.

pipette. It will then be seen that one of these divisions, or hundredths of decimal solution, will precipitate just one thousandth of the quantity that a large pipette of normal solution would do.

A few well-stoppered bottles are required for the solution of the specimens, and carrying on of the operation; and for the heating up of the solution bottles, some convenient form of water-bath, because the dissolved assays clear much more readily if they are operated on at a tolerably warm temperature.

Let it be assumed that the normal and other solutions are all of correct strength, and it is desired to ascertain the amount of silver in a specimen whose quality is quite unknown. Now this quality must be roughly learned before the quantity to be taken for assay can be decided. Thus a rough assay is first made.

As before remarked, the assayer's experience will tell him pretty certainly, from external characters, somewhat of the quality: for instance, whether it be silver of seven, or eight, or nine hundred parts in the thousand.

But in any case, for this rough estimate, an actual, or 10-grain assay pound may be taken, and Vauquelain and other French writers say cupelled to arrive at it. Or it may be done by a modification of the usual wet method. If by the latter, it is to be dissolved in a small quantity of acid. Then, for these approximating assays, it is well to have two or three pipettes of varied capacity, say of 700, 800, and 900 grains contents. If, then, we have assumed from the cut and general examination that the specimen is not less than 900 in value, we take a 900-grain pipette, and add that quantity of normal solution; then well shake until clear. Next, one thousandths of decimal solution (= 10 grains) is to be added as a test, whether the specimen be really above 900 or not. If a cloud is produced, showing that it is so, nine more thousandths, that is, nine such ten-grain quantities may at once be added, which will bring the indication to 910. The liquid is again to be cleared, and another ten thousandths added, but only if the first drop or two (delivered by just loosing the retaining finger from the pipette top) produces cloud; then the whole is put in and the assay again cleared. It is now at 920. The same addition and clearing is again made; and then a fourth: but now this one, which would have brought the assay to 940, is found to be too much; and not only is this so, but it is almost certain that some of the quantity which made the 930 was in excess. Hence it may be assumed that half is to be taken off, leaving the number 925 as an approximation.

Now the calculation for the quantity to be taken for assay of such an approximate value, is one of proportion, thus stated:— As 1000 parts : 925 parts : : 10 grains be to the amount sought, which will be slightly over 10·81 grains. But there are tables calculated for these quantities in all qualities of silver, down to equal parts of silver and alloy.

For the actual assay a quantity rather in excess should be taken, as it is better that some thousandths of decimal salt solution should be required rather than decimal nitrate of silver, from the silver in the assay being unequal to the neutralizing of the pipette of normal salt about to be given to it; therefore the next step would be to weigh accurately two separate assay quantities of 10·85 grains each, and dissolve them. The fumes of nitrous acid are to be blown out of the bottles, and then the dose of normal salt solution got ready for the first, operating thus: the air-valve of the cock being opened, a finger of the left hand is placed below the point of the pipette; the cock is then turned, and solution allowed to flow in until the pipette is full, and it reaches an inch or so above the full mark on the stem; the cock is then shut off, and next the air-valve closed, when the finger may be removed from the beak of the pipette, for as there is no opening above the solution it will be retained without spilling a drop. The level of the salt solution is then very carefully adjusted to the line, by opening the air-valve slowly and cautiously, and thus allowing the excess to drop as slowly into a vessel below. This done, the air-valve is closed, and one of the assay-bottles brought under the pipette. Next the air-valve is completely opened, and the whole of the solution allowed to run into the bottle, leaving the last drop retained in the beak by capillary attraction, as this, being a tolerably constant quantity, needs not to be employed.

The duplicate assay being similarly treated, the two are next well shaken. The French use an apparatus consisting of a divided case for containing some ten assays, suspended by springs, which can thus be put in rapid shaking motion; but for a small number, an assistant will well substitute this. After a minute or so of brisk motion they become quite clear. This shaking acts by breaking up the light curdy structure of the chloride and condensing it, without which it would retain undecomposed argentic nitrate, which would, by more gradual action of the salt, tend to maintain the cloudiness of the solution for a considerable time.

The decimal solution is next brought forward, and a 10-grain quantity added to each assay, these and all additions being carefully noted and registered; if it produces cloud in them, a second is added, and again cleared; then a third, and so on, until an addition of one of these produces no effect.

Suppose, then, that in this way six have been added, the last (taking no effect) would not be counted; then it may be assumed that only half of No. 5 was required, making four and a half thousandths only effective. Now, if the approximation of 925 were really correct, 10·81 parts (the calculated quantity) of silver would have been exactly decomposed by the pipette of normal solution; but as 10·85 were taken, lest the first estimate should have overrated the quality—or, in other words, four thousandths too much to ensure a sufficiency of silver in the assay. We must look to the table, and obtain the actual report in the line of 10·85 weight, and we should there find it, being between the numbers given under the fourth and fifth salt measure columns. It would be actually 925·8, or just above standard silver.

A few columns of one of the tables in use may be here given as an example, and it will be seen from them that, with an approximate report, we can at once learn by such a table the quantity to take for assay, as well as, on the other hand, the actual report from the amount of salt solution added.

1000*th Measures of Salt Solution* (*Decimal*).

Weight of Assay.	0	1	2	3	4	5	6	7	8	9	10
10·65	939·0	939·9	940·8	941·8	942·7	943·7	944·6	945·5	946·5	947·4	948·4
10·70	934·6	935·5	936·4	937·4	938·3	939·3	940·2	941·1	942·1	943·0	943·9
10·75	930·2	931·2	932·1	933·0	933·9	934·9	935·8	936·7	937·7	938·6	939·5
10·80	925·9	926·8	927·8	928·7	929·6	930·6	931·5	932·4	933·3	934·3	935·2
10·85	921·7	922·6	923·5	924·4	925·3	926·3	927·2	928·1	929·0	930·0	930·9
10·90	917·4	918·3	919·3	920·2	921·1	922·0	922·9	923·8	924·8	925·7	926·6

The decimal solution of argentic nitrate comes into use in cases wherein an over-estimate has been made by the approximating assay, and consequently after adding the pipette of normal salt, the first addition of decimal salt solution fails to produce any cloud. Under such circumstances the operator has to work back, adding decimal silver solution just as he would have done salt. The report is shown by the proper table when the assay is done. And there are tables calculated for argentic nitrate measures, just as for the salt; but in the silver ones, of course, the report falls, instead of rising, for each ten-grain addition.

1000*th Measures of Nitrate of Silver Solution* (*Decimal*).

Weight of Assay.	0	1	2	3	4	5	6	7	8	9	10
10·65	939·0	938·0	937·1	934·1	935·2	934·3	933·3	932·4	931·4	930·5	929·6
10·70	934·6	933·6	932·7	931·8	930·8	929·9	929·0	928·0	927·1	926·1	925·2
10·75	930·2	929·3	928·4	927·4	926·5	925·6	924·7	923·7	922·8	921·9	920·9
10·80	925·9	925·0	924·1	923·1	922·2	921·3	920·4	919·4	918·6	917·6	916·7
10·85	921·7	920·7	919·8	918·9	918·0	917·0	916·1	915·2	914·3	913·4	912·4
10·90	917·4	916·5	915·6	914·7	913·8	912·8	911·9	911·0	910·1	909·2	908·3

But assays thus worked back are never so satisfactory as the under-estimated ones, and in practice there is much difficulty in getting them clear after each small addition of silver. Hence Dr. Miller, who largely practised this wet method, advised, in cases where silver is found to be wanting, the addition of five-thousandths of the decimal silver solution at once, and then (presuming it is still not too weak) working forward with salt, and in the end, counting as if these five-thousandths had been at first taken as silver in the assay quantity dissolved.

In conclusion of this matter, it must be borne in mind, that mercury in solution will be precipitated also as an insoluble chloride; and hence, when that metal is present, as it sometimes is, a false report is liable to be given. But when mercurous chloride is mixed with the argentic chloride it is shown by the chloride not being blackened by light, and thus means may be taken to remedy the possible error; but where assays are quickly done this indication is apt to be overlooked. In cases where its presence is ascertained Gay-Lussac advises the addition of a quantity of sodic acetate before carrying out the assay, and then proceeding as before.

In the Indian mints, where unskilled manual labour is very inexpensive, and, moreover, ample time is allowed for the performance of the assays, a process has been perfected by the late Mr. Dodd, whereby he precipitates the silver completely in a light glass flask, by adding at once an excess of sodic chloride or hydrochloric acid to an actual assay pound of silver; the chloride is then patiently washed until quite clean, and decanted with much care into a small porous crucible, where it is afterwards perfectly dried, the manipulation being so carefully carried out as to admit of the removal of the whole of the chloride in a compact cake for weighing. The process certainly has advantages over the French one; it dispenses with approximating assays, and, moreover, admits of a constant weight being employed: but, on the other hand, it is very tedious, requiring much care, especially in the washing operation; although, by the excellent arrangement of apparatus devised by Mr. Dodd, this labour is facilitated as much as possible. Hence it is unsuited where quickness is an object in carrying out assays, although a very simple and accurate wet process.

In the course of the author's own practice, extending over some years, he has been in the habit of employing at need both wet and dry processes, and often upon the same assays, as checks the one on the other, using, of course, equal care in each as to delicacy of manipulation and necessary precautions. Both processes have their advantages, and cupellation very decided ones, while it is capable of great accuracy in practised hands. The variations, as ascertained by pure silver and other standard or proof assays, are always regular and constant, and most easily compensated. It is unfortunate that so beautiful an operation should be undervalued, often, no doubt, from being employed by very unpractised operators, and often also with unfit apparatus and arrangements.

The wet method has its recommendations, the chief, and a very great one, being its easy application where a number of assays of known similarity of composition have to be tried—coin-bars, for example, and so alloyed as to be presumed to be all of an uniform standard. In such all the apparatus, pipettes, &c., may be specially adapted and graduated for their work, and the whole operation on a number very quickly carried out. Thus, the late Dr. Miller, who, as non-resident assayer to our Mint, had the assaying of standard quality alone, has in his *Chemistry* described the apparatus as arranged for such. And if in similar cases the quantity taken for assay is such an one as will dispense with many decimal measurements after the normal one, close results may be arrived at. But where, on the other hand, many decimal measurements have to be made; and from variations of qualities under one and the same set of operations, some assays may require many and other fewer additions, while, perhaps, at the same time the proof assays vary much from the others in such requirement of decimal additions. Then the small errors of measurement which may occur will multiply by their number until the total often becomes a large error, and in such circumstances not an uniform one over the whole. Then, lastly, in wet assays compensation is not done away with; it is equally needed as in dry operations, varying from day to day with changes of temperature and other changing conditions in the solutions, &c. employed; and hence needing also one or more check standards to be worked with the assays as is judged advisable.

CHAPTER VIII.

NOBLE METALS.

GOLD.

IN the early books of the Bible, viz. those of Moses, we find mention not only made of gold, but allusions which show much knowledge of the properties peculiar to that metal. Again, in Job, it is spoken of as dust of gold, and a metal which men refine; while, lastly the prophet Malachi mentions this operation in such terms as to show that it was well understood in practice.

Its use as a medium of value was then a common one, as at the present day, and its domestic applications were also the same, viz. to decoration, not only of buildings, but for ornaments for personal wear; and in many of the ancient descriptions, as for instance, of Solomon's temple, the quantities and uses of the metal seem almost fabulous. Thus, after describing quantities enormous in themselves, we are told that the upper chambers were 'overlaid with gold,'—an expression showing that gold-beating to some extent must have been understood by the Israelites, and we have many evidences that this latter art was practised to perfection by the Egyptians.

Vitruvius again describes the operation of amalgamation in nearly identical manner with our own process.

Gold is found in nature in a state very nearly pure, being associated principally with silver; other metals which are found alloying it are generally only in very small proportion indeed. But the foreign metals associated with it vary, and are peculiar to localities; thus Russian gold often contains platinum; Brazilian, palladium; in Hungary it is associated with tellurium; and Californian gold always contains a large proportion of silver. The beauty of the metal has doubtless always much enhanced its popular estimation; when pure it is of a brilliant rich yellow colour, its colour being capable of much modification by the addition of alloys: thus, by varying quantities of silver or copper alone, we are enabled to obtain various shades of yellow, or even green, as also of red and orange. Gold is commonly used alloyed, for in its natural, or fine state, it is nearly as soft as lead—a property which, although valuable for some of the applications of the metal, renders it incapable of resisting anything like hard wear; and thus in its pure state it is nearly useless for coin or articles of jewellery.

Gold is, with one exception (also of a metal, viz. platinum), the heaviest body in nature. Gold being about 19½ times heavier, while platinum is 21½ times heavier, than water. Gold is very generally distributed in nature; it is found in quartz, running in veins in slaty deposits. This quartz may be of a pure white, but it is commonly more or less stained with ferric oxide from the decomposition of sulphide. The gold is often in the matrix in a filiform condition, at other times in granules, and occasionally crystalline. But a quartz may be largely productive in which there are no manifestations of the presence of gold. Indeed specimens in which it is very apparent to the eye are often very disappointing in their actual produce.

Gold is at times found in granite rocks, but where it is found in largest quantities it is associated with alluvial deposits, produced by the breaking up of primitive rocks, and consisting of sand and gravel. And the origin of such deposits or diggings depends on the disintegration of the rocky matrix brought about in the lapse of time by the action of frosts upon the contained water which thus splitting up the rock, sets free the precious metal, sometimes in the form of minute scales or spangles known as gold dust, at other in large nodular masses designated as nuggets.

The smaller portions are carried down from mountainous districts into the rivers, from the sand of which this dust is commonly separated, being found in largest accumulation at the bends of the streams. From the earliest times, localities of the above nature have been discovered year by year, and although many become exhausted, yet where such older ones still exist their reputation is comparatively lost in the brilliant discoveries of the few late years.

The dust is commonly tolerably free from matrix, but the nuggets are often more or less mixed up with quartz and have an appearance of the metal and quartz having been in a state of fusion together: indeed the nuggets often present this fused appearance, or they look as if water worn and so smoothed upon the surface. Crystals are occasionally met with, at times isolated in the dust, at others jutting out from masses of quartz. These crystals are almost always octohedral, but occasionally in irregular six-sided tables. Besides, these natural crystals, gold may also be artificially crystallised by methods presently to be described.

Nuggets are found at times of very large size. Of two of these which passed under the author's own examination one weighed 175, and the other 84 troy pounds. There was a very small quantity of associated quartz with the former, and none at all with the latter, for on melting it, the loss was but a few grains, indeed no more than would have been the case with an equal weight of refined gold in melting. A very large nugget was shown at our Crystal Palace in 1858, it weighed 145·25 troy pounds, but above all these ranks the famous Sarah Sands nugget of 233·4 lbs. weight. Most of these masses have been discovered at depths varying from ten to forty feet below the surface, but actual quartz mining is now carried on at great depths. Four to five hundred feet or more being a common depth for coming upon such veins.

Gold from the same locality has always a remarkable identity of composition, the amount of gold being very uniform. Thus looking at the gold from some of the early and celebrated Australian diggings; that found at Tambouroura contained about 933 in the thousand; Mount Alexander gold 960, and the Ovens 982 per thousand; and the variation in quality at these and other localities respectively, was exceedingly slight, the nuggets or large masses presenting the same uniformity of composition. Thus a Mount Alexander lump examined by me gave 961 of gold, and others ranged between this and 965 parts in the 1000.

The range of quality of Australian may be taken as between 930 and 983 parts gold in the 1000.

Californian gold is of much lower standard, the greater part being of from 865 to 890 per 1000, but it rises at times as high as 930; the alloying metal is principally silver, and the same remarks hold good as to composition. Again the other associate metals of both Australian and Californian gold are mainly copper and iron. Some analyses may here be given of each of these varieties:—

Australian.

	1.	2.	3.	4.	5.	6.
Gold	992·5	982·0	956·9	953·3	950·4	946·4
Silver	6·5	11·0	39·2	40·3	37·6	49·5
Copper	...	...	...	6·0	...	4·1
Iron	...	...	1·6		...	
	999·0	993·0	997 7	999·6	988·0	1000·0
Analyst:	Claudet.*	Makins.	Henry.*	Makins.	Makins.	Makins.

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* Phillips' *Mining and Met. of Gold*, page 3.

Californian.

	1.	2.	3.	4.	5.	6.
Gold	865·7	887·0	891·0	901·2	927·0	930·0
Silver	123·3	107·0	105·0	90·1	69·0	67·0
Copper	2·9	6·6	...	8·7	4·0	...
Iron	2·4		2·0	...	...	...
	994·3	1000·0	998·0	1000·0	1000·0	997·0
Analyst:	Henry.	Makins.	Rivot.	Henry.	Levol.	Rivot.

As to localities, all quarters of the world produce gold; and in Europe, even our own country has afforded small quantities. Thus, from time to time it has been met with in Cornwall, in steam works where tin-mining is carried on. At Coombe Martin, near Ilfracombe, in Devon, from 300 to 400 persons were, at one period, employed in actual gold-mining, and it has been stated with very large produce, but the statement is doubtful. Then, in Cumberland, Scotland, and Ireland, it has been found.

In Lanarkshire, in Scotland, 300,000*l.* worth was procured during the reigns of James IV. and V. of Scotland; and at Wicklow, in Ireland, the peasantry who discovered its existence gathered some 10,000*l.* worth. Mallet (*Phil. Mag.*) gives an analysis of the gold-producing river sand of Wicklow as containing 923·2 gold per 1000, together with 61·7 of silver, and 7·8 iron.

About ten to twelve years since the North Wales districts began to be fairly worked after failures previously, and for some time the Vigra, Clogau, and some other mines promised some yield, but the success was very slight; and Phillips states that the total yield 'from the commencement of operations in the North Wales gold district up to April 1st, 1866,' was the very moderate amount of 12,800 ozs. But that 'Some further discoveries of gold at Vigra and Clogau have been recently announced.' Indeed, in all the places just named there has never been any practical production of gold, and, as they may have just about paid their expenditure, they have afforded a tolerably safe outlet for such spare capital as is always forthcoming when asked for from those fond of such speculative investments, whose history has generally been that of partial success sufficient to tempt, but as generally followed by failure in the end.

Analyses of two samples of gold from the Clogau mine, and also one of gold dust from the bed of the River Mawddach, have been published by D. Forbes:*—

	Clogau Mine.		River Dust.
	1.	2.	
Gold	90·16	89·83	84·89
Silver	9·26	9·24	13·99
Iron	trace	trace	·34
Copper	trace	0·0	trace
Quartz	·32	·74	·43
Loss	·26	·19	·35
	100·00	100·00	100·00

The specific gravity of No. 1 was 17·26; and of No. 3, 15·79.

On the Continent, small but unremunerative quantities have been found in France, Spain, Switzerland, and the Rhine districts. But Hungary and Transylvania actually produce about an average of 70,000*l.* worth yearly, from several mines.† In some of these mines the gold is associated with argentic sulphide, in others with auriferous iron pyrites. And together with these the important adjunct of galena, whose lead is of the greatest use in smelting these ores. All the Transylvanian ores contain tellurium.

In Silesia some old mines have been reopened a few years since, and, although poor, worked to much advantage by a process which will be hereafter described.

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* *Phil. Mag.* Nov. 1867.

† Phillips gives their joint produce for 1865 at 5395 lbs. troy, which would be of about 269,750*l.* value.

In Asia, Russia is the only country producing gold. And the late Sir R. Murchison states its present produce at about 3,000,000*l.* per annum. The mines in the Ural and Siberia contain the metal in auriferous pyrites, and Russian gold is often also associated with platinum and palladium. The largest amount is procured from the high ridges of Siberia, which separate it from China. In the Ural it is separated from a quartz matrix obtained in deep mines sunk in the rock itself. The chief mine is that of Berezovsk, at Ekatherinburg, but the quantity obtained is small in comparison with that from gold-washing operations in the neighbourhood of these districts, where alluvial deposits containing a large amount of gold have been transported by the agency of water, detaching them from their original position, and carrying them to places where they are obtained.

Phillips says the gold in the material operated upon does not now amount to more than four to six parts in a million, and but for the efficacious washing machinery employed it could not be worked at any profit.

An analysis of the quartz gold here, by Rose, gives the following composition,—gold 918·8, silver 80·3, copper 0·9, iron a trace.

The same analyst gives the gold from the sand washings near Ekatherinburg as—gold 989·6, silver 1·6, copper 3·5, iron 0·5.

In India the yield is not very large.

In Africa Ethiopia furnishes the present supplies, where the metal occurs in ferruginous earth in spangles; and thus all the African gold received by us is in the form of dust, and obtained from washing alluvial soils upon the borders of rivers, as well as from the ferruginous earth and sand dredged from the beds. These are chiefly hand washed by the natives, this being dexterously done in wooden bowls.

In America, Brazil in the south furnishes a large supply now, and in Mexico large quantities are yearly separated from the silver there obtained. From the years 1600 to 1700 our sole supply in Europe was from South America, and during that century 337 millions worth of the precious metals was furnished hence. From the Brazils the gold supplied is from the same soil as the African. English companies work the deep mines here: one of these, the Morro Velho mine, of the St. John d'El Rey Mining Company, is worked on a very extensive scale; the ore is stamped, then powdered in an arrastre, and subsequently amalgamated in barrels. The raw material affording about half an ounce of gold per ton. Levol's analysis of Brazilian gold is,—910 gold, 87 silver, 3 copper and iron. New Granada, Peru, and Chili, produce a considerable amount. In our British possessions of Canada and British Columbia gold is found; in the former, from shallow digging chiefly in the neighbourhood of the Chaudière River, and there is every prospect of considerable produce from the deep quartz mines now entered upon there. In British Columbia the large yields have been from Cariboo. These golds much resemble the Californian in containing a large amount of silver. An analysis of Canadian by Hunt gave—gold 864·0 to silver 136·0. And of Cariboo gold by Claudet, 842·5 gold to 149·0 silver.

The chief American yield is from the North, and there from a small slip of country in its south-west limit, viz., from California. The Sacramento River, and small streams flowing into it, are the productive localities of that country; the gold district extending to the Bay and Town of San Francisco. It is here found in deposits formed by the disintegration of quartz and granite, and in the valleys and flats the gold is mixed with gravel and boulders, these latter being formed of quartz.

The Californian gold is principally carried to the States, where it is refined, and our supplies from the former country thus come second-hand to us, and generally as refined gold. Although the existence of gold in California was known some years before, yet it was not until 1848 that the fact was turned to practical account, and the collection of the metal really commenced. Phillips estimates the first year's produce, viz., 1848, at 10,000,000 dollars.

This increased to 65,000,000 in 1853, and thence as steadily fell again to 26,500,000 in 1866. He says the produce of these nineteen years had a value of 836,00,0000 dollars (= 174,166,666*l.*). One-third being from quartz mining, and the remaining two-thirds procured from shallow deposits and hydraulic mines, that is to say, from washing down the banks of earth wherein the metal is found by means of strong streams of water directed upon them by a hose; the water being brought from neighbouring lakes by canals, into proper receptacles for the purpose.

The quartz mines in California are worked to a great depth, one of the chief, viz., the Eureka, is about 400 feet deep.

About four years after the discovery of the Californian mines the Eastern Australian gold fields came to light, the information being first practically afforded by a Mr. Hargreaves, in April 1851; but it had been prophesied some ten years previously by the Rev. W. Clarke, during some geological explorations, and again, in 1851, by Sir R. Murchison.

When first found here, the quantities obtained at Ballarat and other places were so fabulous, that it is not very surprising that Australian society was almost in a state of disorganisation, or that so great a sensation was created in our own country that a continual rush of all classes of persons emigrated to the colony. For it was not uncommon for diggers in one week to obtain from 1000*l.* to 1500*l.* worth of gold by ordinary working; and in one case, well known to the author, a party of three obtained 20lbs. weight of gold dust in one day. Then, again, as a rarer example, three English sailors, who were digging with pretty good general success, at the close of one day's work came accidentllay down upon the nugget, already mentioned, which weighed no less than 175lbs. and was by them brought to England for sale.

The gold here is always more or less associated with quartz, and generally lies upon a yellowish-brown rock, being found at depths varying from 14 to 40 feet from the surface. It is maintained by some, that at great depths there are unlimited supplies, and that the gold found in alluvial deposits and rivers has, in all probability, been deposited there by volcanic action. And upon this theory operations were soon experimentally made in Australia for deep quartz mining, and at the present time some quartz reefs are worked to 500 feet in depth or even more, and and with no decrease in their yield.

Victoria has been the chief producer of gold; indeed far beyond any other part of Australia, and here, as at all diggings, it was obtained rapidly at first by surface-work, but as diggers increased, and surface material was exhausted, so working became deeper and deeper, until at the present time it is chiefly deep quartz mining that is carried on; and this is especially true of the once famous diggings of Ballarat and Bendigo, where the whole soil, abounding as it did in the precious metal, has been removed for its extraction, until the quartz rock is now being worked. The cost of working per ton is according to Phillips about 16*s.* 4*d.* at Victoria; and he says that it is although fluctuating highly remunerative, and 'presents an attractive field for the investment of capital in this department of industry.' The year 1851 was that in which the great influx to the colony of Victoria took place, and gold digging was the pursuit of all, and was more or less fluctuating in produce and yield. In estimating the quantity of gold obtained, it will be fairer to take a period, say of ten years' production from 1854 to 1864. During this period about 25,875,345 ozs. were shipped, which at 4*l.* per oz. (a fair average price for Australian gold) would amount to 103,501,380*l.* But in this calculation, no estimate is attempted of small amounts retained by their owners, and also of quantities transmitted elsewhere; nor indeed of the large amounts coined in the colony for home use there, which together would very considerably swell the estimate above made.

Although gold was discovered in New Zealand in 1842, it was not until about 1858 that any really practical move was made in gold-mining there; after which time small quantities were obtained in England from thence at intervals. But in 1862 and 1863, so many encouraging discoveries, both as to localities and produce, were made, that the colony began to be looked upon as ranking high in the gold regions of the world. The province of Otago is the chief amongst a number of other places. It is here obtained from alluvial soils, and from river workings. At the present time quartz-mining is also carried on, and at Waipori more particularly, and from advices received during the past year the prospects of yield from quartz working are exceedingly good. The New Zealand yield may be roughly estimated at about 500,000 ozs. annually.

Phillips gives a useful table of the gold production over the world.* In this he shows the total production for the year 1800 as being 53,940 lbs. troy, for 1850, 345,250 lbs. for 1860, 585,370 lbs., and for 1865, 559,587 lbs. Then taking the latter year and calling the total yield 1000 parts, of this California and the neighbouring States yielded 375 parts; Australia, 279; the Russian Empire, 124; New Zealand, 74; Chili, Bolivia, Peru, New Granada, and Brazil jointly, 61; Southern Asia, 45; British Columbia, 21; Austrian Empire, 10; Africa, 7; and Nova Scotia, 4 parts.

The operations of the Australian gold-digger will show how much the working of gold-mining is purely mechanical; for in the shallow diggings the metal is associated with alluvial materials, such as clay, gravel, sand, &c.; and as these vary very much in specific gravity, they need but some judicious method of treatment with water, completely to separate the heavy metal from the lighter earthy matters.

In early times of newly discovered gold districts, a party of diggers, after opening the ground, commence operations by what they call 'prospecting' the soil. This is effected by taking up portions in a shallow basin, and adding water; then by well shaking, the earthy portions may be suspended, and ultimately washed off. The portion of metal left in the bottom of the basin, if any, shows them whether the spot is rich enough to pay the working. The metal was usually found largely upon or very near to the surface, but at times covered with sand or gravel so as to need some excavation, and hence the operations of the digger, although carried out occasionally singly, were so done at disadvantage, and therefore a party of two, three, or even four, worked more economically. Supposing then the selected spot be promising the digging is carried on, and the earth either washed in the basin just mentioned; or else if the party consists of four or more men, a machine called 'a cradle' is employed. This is a long trough of some 7 ft. in length, and 2 broad; across the bottom of this several bars are nailed at equal distances, and at the upper end a kind of sieve is fixed at about a foot above the bottom. This whole arrangement is mounted upon rollers.

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* Phillips's *Mining and Metallurgy of Gold and Silver*, page 127.

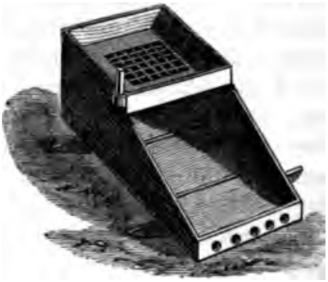

Fig. 55.

One man digs out the earth from the hole, a second supplies the cradle sieve with this auriferous earth, a third keeps up a supply of water, which he pours upon the earth in the sieve, while a fourth keeps the machine continually moving upon the rollers. The large stones washed out are removed by hand from the sieve, and the water, at the same time, washes the smaller through, which is slowly carried towards the lower end of the trough by a slight inclination being given to the whole. Thus the flow of water tends to keep the earthy particles in suspension so as to allow of their washing off, while the heavier portions of gold are obstructed in their flow, and retained against the cross bars fixed to the cradle bottom. These are removed from time to time and dried in the sun, when, after blowing away lighter particles, the metal only further requires to be melted.

Such was the simple operation where no clay was mixed with the material, but most of the Australian fields abound in stiff clay, hence a preparatory step is needed to disintegrate this and free the metal, &c. This is effected by washing the dirt in a large puddling tub, which is half filled with the material, and water then baled in. It is then constantly stirred with shovels or some revolving arms until the clay is diffused, and the metal and stones set free, after which they are cradled.

The 'pay dirt,' as it is termed, is followed to various depths, and I remember questioning a digger who was having some 300 ozs. of dust melted, as to the position in which he had found it. He had worked single-handed, and as he said in rather a cooler place than the melting-house, for he had obtained the bulk of it at a depth of 20 feet in a small hole, and up 'to his waist in mud.'

A single-handed digger will sometimes wash entirely with the pan, throwing in the puddled material, and then by giving it a dexterous motion with water, something between shaking and rotation, will manage to pour off smaller earthy particles, so as to be able to separate the metal from the larger. In all cases a large quantity of water is needed, every hundredweight will require fully 50 gallons of water. Where the dirt is very rich and water scarce, the former is frequently separated by land; after hand breaking up well, the stony and earthy parts are picked out, and then the last and lighter portion blown away so as to leave the metallic portion alone.

In cradle-washing the riffle bars across the bottom of the cradle forming the retaining angles for the metal, are liable to be levelled by the sand, flowing over, and thus the obstructing angles done away with; hence they must be cleared out from time to time during working or there will be much waste from the flowing away of smaller particles of metal, and thus much of the refuse of the early Australian diggers, who worked when the yield was most profuse, has been again worked with considerable profit.

The operation above described is in principle just what is carried on in all localities where gold-dust is collected, the differences being only slight ones of manipulation.

Thus in some of the river-washings the sand is raised from the bottom much in the way that ballast is dredged from the Thames. The sand being received in boats is then hand-washed in small wooden bowls, just to a certain point of cleansing; beyond this, as the metallic particles are very fine, loss would arise from their pouring away with the smaller sandy particles; so the produce is finally washed in vessels or tubs upon the shore, after which the whole residue is treated with mercury, which amalgamates with and dissolves the gold, so as to admit of the final separation of foreign matters: the amalgam being finally heated to distil off the mercury.

But the chief supply of gold is now obtained by the more systematic working of the quartz rock containing it. This is subjected to crushing, and is afterwards stamped and ground to powder. This powder is then treated with mercury, and from the amalgam obtained the gold subsequently separated.

But mercury is also, at times, employed in the separation of gold from the ordinary washing dirt, for not only may the ordinary mechanical washing fail to separate particles of metallic bodies having a tolerably high specific gravity, but at the same time very fine particles of gold may, from their small or scaly form, be washed away. For these and other reasons what is termed sluice-washing is often resorted to. The sluice is formed by a series of wooden troughs of about 10 to 12 feet long; each one placed at a slight inclination, its lowest end passing on to the higher one of the next trough so as to deliver the stream fairly upon it. At intervals retaining bars for the metal, mercury, and amalgam, are fixed either crossways, or at varying angles to the sides. These are called riffles. In using the arrangement, the dirt is shovelled on at the top of the first trough, and then a good stream of water kept flowing down to disintegrate it, and wash it on down the course of the sluice. After a time the requisite quantity of mercury is poured on at the upper part, which flows down and is retained in the angles formed by the riffle bars. Any larger portions of gold, or large stones, or quartz boulders, are removed by hand or separated, the smaller portions of precious metals flowing on to the mercury, amalgamate with it; while the earthy portions of the stuff wash down from division to division, until at last they flow off as mud or 'slimes,' all but, if not entirely, free from gold, if the arrangement has been good as to length, slope, supply of water, and of mercury. The arrangement is separated from time to time; the amalgam and metallic portions recovered, and the whole cleansed from earthy matters, and again put together for use. In order to ensure retention of all, and especially of the very minute portions of gold, as also to save mercury, a large amalgamated copper-plate is at times placed upon the floor of the trough, so that the washing waters shall pass over it; this usually retains all the smaller particles, which thicken the adherent mercury. When this is the case the plate is removed from time to time, the thick amalgam heated off, and some fresh mercury put upon it for further working in the same way.

In the working of gold-quartz the first step is, of course, crushing, so as to liberate the enclosed metal, and in the earlier machines, as those of Berdan, Perkes, and others, this was effected, and amalgamation simultaneously carried on. These machines were but modifications of the Mexican arrastre (see fig. 32), which is often employed in gold mining also, and in all these the mercury is put into the machine, so that while grinding amalgamation is at once effected. Berdan's mill was an iron chamber in which some iron balls rolled round an axis; and Perkes's differed only in his employing cones for balls, the cones revolving on their side, their apices pointing inward toward the centre.

But the more common practice is to break up the quartz, first coarsely, and perhaps there is no better machine for this first operation than the one here figured.

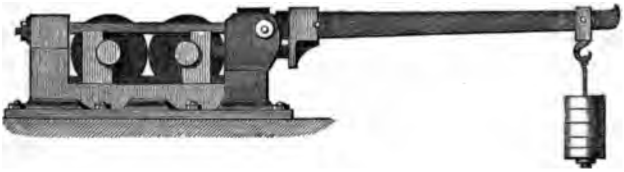

Fig. 56.

It consists of two rollers of cast-iron, moving as in the ordinary flatting-mill, but in perpendicular bearings, which by sliding in a groove on each side, admit of the adjustment of rollers as to distance apart. A long lever acts upon the bearings of one roller by its own weight, joined to that of a tolerably heavy one suspended upon it. It presses the roller forward, and also allows of a little separation, so that pieces which resist breaking, from their size or hardness, will pass through. This elastic power also admits of regulation by adding to the weight, or removing it nearer or further from the end of the lever. The crushed matters pass through a strong sieve, so as to separate the large portions for a second crushing. The finer parts are then stamped, in similar stamping-mills to those used in the Mexican silver-works. In the single stamp here figured, *a* is the iron chest in which it works, *b* the stamp head, of iron, also, *c* the shaft on which the boss, *d*, is placed in order that it may be lifted by the cam, *e*, placed on the motion axis of the machine. These cams are so ranged round the axis as to lift the stamps alternately; for a series of stamps are arranged in each mill, side by side, generally five to each battery. The stamps are required of considerably heavier weight for gold-quartz than for silver ores, hence they are seldom less than 5 cwt. each, and may range up even to 8 cwt. A grinding motion is sometimes obtained by causing the stamp in descending to rotate partially as it falls. Mercury for amalgamation is, at times, put into the stamping-mill, but more commonly this operation is effected in a separate apparatus; and any finer grinding, if found needful, is also done in the machine where the amalgamation is carried out.

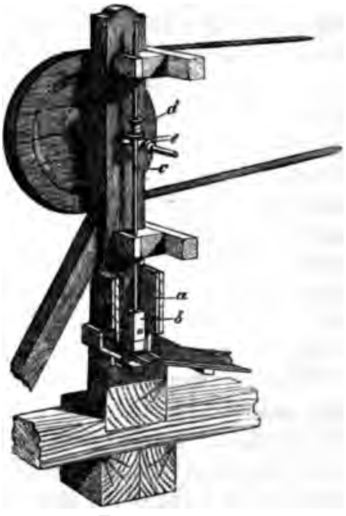

Fig. 57.

Some washing is necessary, especially if the quartz be poor, in order to get rid of valueless portions, and thus concentrate the gold, and bring it more under the influence of the mercury. It is usually performed upon blankets stretched upon a frame. At one of the Welsh mines, the Cwneisen, the first blanket was 11 feet long, and about 16 inches wide, with one inch fall in the 11 feet. The material then passed to a second of 7 feet long, but almost all the gold was retained upon the first. If these blankets are used too wide, in proportion to their length, it is not easy to make the water flow uniformly over the woollen surface. After a time of working the blankets are removed and washed in a tank, so as to remove the more auriferous material, which if allowed to remain too long without removal, completely obliterates the woollen fibrous surface, and so defeats the intention of their use. But in the use of these blanket-boards, there is always a certain portion of metal in so fine a condition as to wash throughout the length, and which would finally escape, without some further means of retaining them ; for this object, therefore, amalgamated plates are again (as in ordinary sluice-washing) often placed at the end of the arrangement, in passing over which these smaller portions are arrested and retained by amalgamation. Lastly, there is always a quantity of fine matter in the state of iron sulphides, which washes off, but yet contains a notable quantity of gold, and is therefore retained and reserved for further treatment.

The next step is the amalgamation of the gold in this ground and concentrated material, and many forms of apparatus are in use for this purpose. The requisites being a certain amount of grinding power, sufficient speed to stir well, and also some centrifugal action, so as to aid amalgamation. And the mercury should be so disposed as to avoid, as much as possible, too much grinding action being exerted upon it, for 'flouring' of the mercury, that is, bringing it into too fine a state of division, is to be avoided.

A very excellent amalgamating apparatus is in use, which will well illustrate the requisites of such a machine. It consists of a series of cast-iron pans, mounted upon separate strong tables, and arranged one above another, at such heights, as that when the first one is filled, any overplus flowing into it may flow by a spout into the second, and similarly from the second into the third, and so on. The centre of the casting is carried up in a tube which is arranged so as to allow of the passage of the axis of the moving part of the machine up this; this axis is centred below in the base of the machine; just above the centre is placed a large toothed wheel, which engages and drives a similar one on the second, and so on throughout the series. To the upper end of this axis is fixed an arm, or collar, from the circumference of which pass down iron rods, and to the lower ends of the latter a large wooden muller is screwed; this has externally the form of the interior of the iron pan, but internally it is turned out conically, or basin-shaped, to a centre hole, which admits of rather more than the passage of the central tubular part of the basin; on the under side of this several projecting pieces are fitted, which nearly touch the bottom of the basin.

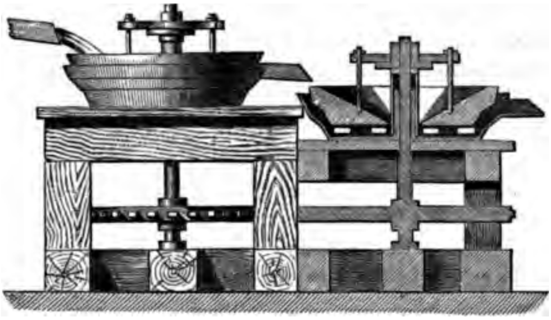

Fig. 58.

The machine is thus used:—Mercury is put into the outer basin, to the extent of about half an inch in depth, then the auriferous material (which in the localities where these machines are employed is an auriferous iron pyrites) is made into a kind of mud with water, and allowed to flow into the first, or upper machine by a spout being conducted into the centre cavity of the muller; passing down through the centre opening, it comes in contact with the mercury, and by rotation is well mixed up with it; the apparatus filling, it overflows and passes by the next spout into the second, where the same operation goes on; and thus, in like manner, through all the set, all being charged first with mercury. Thus the particles of gold are dissolved in this mercury, and the operation is continued, but still employing the same metal in each machine, until it has taken up about a third of its weight of gold, and begins to lose its fluid state. The mercury is then drawn off, and all excess squeezed away by pressing it through leather bags; thus a semi-solid amalgam is obtained.

Phillips describes and figures a very simple apparatus for amalgamation employed in California, and contrived by Mr. Attwood.*

At the upper part of an inclined plane of about 9 feet in length is a trough, above which is placed a hopper for containing auriferous sand (washed). Crossing are placed two rollers of wood, each about 8 inches in diameter by 2 feet long; these revolve by bands and pulleys in the same direction, but contrary to the course of matters flowing over the arrangement. Upon their circumference are fixed a number of slips of iron, which, like knives, work in a cistern of mercury during revolution of the cylinders. In use, the washed auriferous sand is allowed to pass in from the hopper, and with it a stream of warm water; thus it is carried under the rollers, and by the arms stirred in contact with the mercury. It then traverses the inclined plane or riffle board, which latter is divided into several channels, and provided with movable plates of amalgamated copper, to which the gold amalgam formed as above, can attach itself, and be removed from time to time; while the surplus material flowing off and yet containing some gold, is reserved for further treatment in fitting apparatus.

This amalgam may be distilled in a precisely similar way to the silver amalgam described already. The common method of treatment consists in squeezing it into masses, and introducing into any convenient shaped retort, and there is none better than a flanged iron crucible. The amalgam is put in this, and a cover

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* Phillips's *Metallurgy of Gold and Silver*, page 184.

provided with an eduction pipe fixed on and luted. This pipe passes to a vessel of condensing water, and is carried into it by means of a canvas tube passing under the surface; this elongation acts as a safety-tube, to prevent the water flowing back into the retort in case of accidental vacuum forming therein.

The retort is plunged into any ordinary furnace, and heat carefully got up, the temperature being kept down to that which will just distil off the mercury, without any partial fusion of the spongy gold; for if the latter occurs it is sure to stick to the rough surface of the iron retort; but to guard against this accident it is better before charging in, to smear the interior over with wetted fire lute, as also to keep the heat below dull redness. Indeed, to thoroughly free the spongy amalgam from the last traces of mercury, a long-continued low temperature is needed; a higher and quicker heating, contracting the sponge too quickly and rendering it liable to retain traces of mercury.

The gold is thus left associated with the non-volatile alloys which existed with it in the quartz, and occasionally also with traces of retained mercury, where the retort operation has been carelessly carried out. It is now ready for melting, during which operation these traces of mercury may be driven off.

The melting of the metal into bars is an operation which requires some skill and experience, more especially where the material operated upon is gold-dust obtained by mechanical washing. For this latter is often mixed with small quantities of foreign metals which would, by melting with the gold, much destroy some of its characteristic and valuable properties. Some of the finer qualities of the Australian gold have often small portions of tin and antimony mixed with them, sufficient to render some refining operations necessary before working, but which, by proper precaution in melting, may be got rid of without. In the melting-house the pots generally used are of black-lead ware, for the molten metal is both dense and valuable, hence a fractured pot is a serious matter, and one which is sure to occasion more or less loss. These pots should be annealed before using, by turning them mouth downwards in the fire. The dust is then put into a copper scoop and from it poured into the pot, the latter is then put into the furnace and heated up; this part of the operation should not be hurried, but the metal got into good circulation, and then carefully stirred with exposure to the air. If there is any expectation of such metals as those mentioned being present, a little nitre may be added as a flux for their oxidation. Borax, too, is generally added, and after all, a little bone-ash to cleanse the surface. Lastly, the metal, being well fluid, is to be poured into a greased ingot-mould.

The bone-ash acts as an ordinary sponge by absorbing other liquid fluxes (as borax), and with them any impurities they may have dissolved.

Amalgamation is sometimes found difficult to effect in some cases where the surface of the gold is altered, from the presence of bodies like arsenic, tellurium, or sulphur especially. The presence of the smallest trace of sulphur has lately been shown[*] experimentally to quite prevent amalgamation, as it combines with the gold, giving it a surface of auric sulphide. In such it has been proposed to add to the mercury to be used a small quantity of an amalgam of mercury with sodium. Wurtz, of New York, and Crookes, of London, appear to have made this discovery about the same time; and both find that somewhere about 4 per cent of sodium combines with mercury into a hard, brittle amalgam.

Wurtz's amalgams are simply mixtures of the two metals and in the proportions of $2\ \mathrm{Na} + 98\ \mathrm{Hg}$, and of $4\ \mathrm{Na} + 96\ \mathrm{Hg}$, and in using, one or other of these qualities is dissolved, in the proportion of one part of it to 100 parts of mercury; or even in smaller proportion. By this addition the mercury is said at once to adhere to metals, which would not even have been wetted by it, if used without the amalgam.

Crookes employs three kinds, and designates them as A, B, and C amalgams. In each, he uses the same quantity of sodium, viz. 3 parts per cent. Thus his A amalgam is 97 mercury to 3 sodium. B is 77 of mercury to 3 of sodium, but with 20 of zinc;

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[*] Skey, *Chem. News*, 23, page 277.

and C is 77 mercury to 3 sodium, with 10 of zinc and 10 of tin. Crooks' method of making them is as follows:—He beds a strong iron flask, having a small neck, nearly up to its mouth in a sand-bath, and then heats it to 300° F. = 149° C. Having put the weight of mercury into the flask, he adds the sodium in pieces of the size of a pea, and as violent action follows each portion, after adding a lump, he waits till it is over before each fresh addition. In dropping the sodium in with tongs, the hand being covered with a cloth, a slight explosion is heard, and flame issues from the mouth, which lessens as the mercury becomes charged with sodium. When the quantity has been added, the contents of the flask are poured out on a flat dish, and when cold, the cake is broken up and preserved in a well-stopped bottle. Naphtha is not needed for its preservation. It forms a mass of brilliant, needle-shaped crystals, having but slight cohesion. In forming B, half the mercury is combined with the sodium as before. Then the zinc is separately melted, and just before solidification the other half of the mercury is added to it, with constant stirring. Next, the two are fused together, stirred with an iron rod, and cast as desired. C is made as A, but with the zinc and tin added in the first instance.

Calvert has proposed to separate gold from quartz by solution of the former in chlorine gas. For this purpose he finely powders the quartz, and mixes it with 1 per cent manganese oxide. These are put into a vessel with a false bottom, the latter perforated with holes. The chlorine gas is then passed through it for 12 hours. Water is then added continuously, so as to percolate the mixture, and carry the metallic chlorides into the false bottom. After adding the liquid several times to the ore, it is separated, and iron added to precipitate the copper; after which, the gold is thrown down by ferrous sulphate.

If the ore contain silver also, then, for generation of the chlorine, sodic chloride, manganese binoxide, and sulphuric acid are used, thus argentic chloride is formed during the reaction, which is dissolved by the excess of sodic chloride. The silver is then first separated, and afterwards the copper and gold as before.

Mr. Longmaid has patented a process for the separating of gold by means of plates of iron. For this he powders the quartz and mixes it with roasted pyrites, ferric oxide, limestone, and fluorspar. This mixture is smelted in a reverberatory. Thus, much of the gold subsides, but some remains mixed up with the slag. An iron plate is now dipped through the latter, when gold will adhere to it; the red-hot plate is withdrawn, and plunged into a bath of melted lead; this dissolves off the gold. The plate is then again put into the furnace, and the operation again repeated until all gold is withdrawn. It is subsequently separated from the lead by cupellation.

Hitherto we have considered gold as found either in dust or associated with quartz; but there are sources of the metal in poor ores, wherein it is associated with silver, with tellurium, and even in yet smaller proportion with the sulphides of lead, iron, and copper. Now any of these may be worked profitably by a plan already described as applicable to poor silver ores, namely, by fusion with lead or litharge, or even with plumbic sulphide, and thus an alloy of gold and lead, with any silver present, is formed. This mixture would then be ready for cupellation, whereby an alloy of gold and silver would be obtained.

But it is often necessary before fusing with lead to concentrate the gold to some extent in poor ores. Thus, in Hungary, a pyritic quartz containing a very small amount of gold is first roasted, for the purpose of oxidizing some portion of the ferric sulphide, as well as for the reduction of another portion into ferrous sulphide, by driving off a proportional of its sulphur. This done, some flux is used to separate the quartz, and that portion of the iron which has been oxidized; and lime is thus employed for the purpose. Heating the mass with it, it takes these bodies, and with them forms a slag which covers a matt of richer ferric sulphide. This latter is next removed, and the operation again carried on upon it, with the addition of a little more of the ore and some fresh lime, and this is repeated until the resulting matt is considered to contain sufficient gold for its final treatment by fusion with lead. This separates and takes the gold, subsiding with it under a layer of ferric sulphide. It now only remains to cupel the gold lead in order to recover the former.

It has been already stated that some old gold mines in Silesia had been reopened, and worked with a profit. This has been done by a very clever process, devised by Plattner, and described by him in the Jurors' Report of the Great Exhibition of 1851. It is thus practised: The ore which is ferric sulphide, containing also some arsenic, and about 200 grains of gold in the ton, is first heated in a reverberatory furnace. The arsenic is thus driven off, and condensed in a proper chamber as arsenious anhydride. The residue is removed, and put into a vessel, where a current of chlorine gas can be passed through all. Thus the iron and gold are both taken up in the state of chlorides.

The mass is now treated with water, which dissolves these out, and through this solution dihydric sulphide is passed, which precipitates the gold, the precipitation of any of the iron being prevented by the addition of a small quantity of hydrochloric acid.

A quantity of sulphur is sure to precipitate, by the decomposition of some of the gas; but on separating the auric sulphide, and heating it, all the sulphur is driven off.

Although Plattner advises the use of H_2S for the precipitation of the gold, it would be equally well separated from the solution of mixed chlorides by means of ferrous sulphate, when it would go down as metallic gold.

The gold obtained by any of the means already described always contains more or less silver, as also, at times, copper, traces of iron, and other metals. Hence, for some purposes, it is subjected to an operation called 'refining,' which term is usually applied to a wet operation, wherein acid is employed as a separator. But before passing to this, the American process of cementation may be described, as an example of dry methods of parting.

The alloy of gold and silver is granulated, and a portion, of an inch or so in depth, is put into a crucible; upon this a layer of cement, formed of one part of sodic chloride mixed with two parts of brick-dust, then another layer of the mixed metals, and so on alternately, until the crucible is full. The pots are then covered, placed in a wood fire, heated to dull redness, and kept at this for 24 hours. Under the conjoined influence of watery vapour, furnished by the wood, which passes into the mixture through the pores of the crucible, and the silica of the brick-dust, the sodic chloride is decomposed. Its sodium derives oxygen from the decomposition of the water, and soda is formed; this combines with silica, forming sodic silicate. The liberated chlorine of the salt, with the hydrogen of the water, forms hydrochloric acid, which, at the temperature employed, furnishes chlorine to the silver, to form argentic chloride; this fuses, and is absorbed by the brick-dust, so as to allow a fresh action upon the metal, until in this way the gold is nearly freed from the silver it was alloyed with.

This method effects however but a very partial refining.

Kerl states that a cementation operation of this kind is used at times in order to make 'gold much alloyed with silver appear as fine gold.' The alloy is heated (after rolling thin) for twelve to eighteen hours with the cement-powder; the temperature being kept only just below the melting point of the alloy. The powder used is a mixture of one part of sodic chloride, one part of alum, one of calcined ferrous sulphate, and three of brick-dust. The heat sets free sulphuric acid from the sulphates, and then chlorine from the sodic chloride. The use of the brick-dust is merely to render the mass less dense, and augment its volume. Argentic chloride is found on the surface, and absorbed and so removed by the cement-powder.

But the wet refining, or parting operation, is by far the most advantageous process, and is therefore the chief means employed here and also on the Continent. This is performed by acting upon the granulated alloy, either by nitric or by sulphuric acid.

By nitric acid, the gold is not as a rule left quite so fine as by sulphuric, but on the other hand the oxidizing qualities of nitric acid give it great advantage in refining gold from such metals as antimony, and other equally injurious ones. From the closeness with which sulphuric acid will act, the refining process may be carried on profitably, employing silver containing very small quantities of gold. Thus in France it was found very remunerative to separate the gold from old five-franc pieces, which contained only one to two thousandths of gold, and it is now well known that silver containing only half a thousandth may be very profitably refined.

The refiner, in the purchase of metal for his operations, endeavours to obtain gold containing as much silver as possible; and as this requires fusion with silver for the carrying out of the operation, it is of course an object to employ silver which contains small portions of gold, and thus, as it may be said, to carry on a double refining operation at once. As the actual separation of the two is effected by boiling the mixture in an acid, which, while it is a ready solvent for other metals, is yet inactive upon the gold, it may be said,—why not at once treat the silvery gold with acid, without such alloying? This would be quite useless, for the foreign metals being in so small a relative proportion, the acid would only remove the alloy at or near the surface, the metal being sufficiently close in texture to mask all the rest from the action of the acid. The refiner, then, as a first step, has rough assays, made of the relative quantities of gold and silver in his two metals, after which he makes a mixture of them in the proportion of two parts of silver to one of gold, or at times as dilute as three of the former to one of the latter. Hence the term 'quartation' used to be applied to this mixing. These proportions are fused together in black-lead crucibles, well mixed, and then poured out into a tank of cold water, so as to granulate the metal. It is then ready for the acid.

Formerly the boiling in acid was effected in glass mattrasses, but as much loss was at times experienced from their fracture, as soon as the manufacture of platinum was effected, it was brought into use for these operations; and although a moderate-sized digester will cost somewhere about 1000*l.*, the expense is quite counterbalanced by their saving in working.

The granulated alloy is now put into the digesters, which are furnished generally with long stoneware condensing pipes, the latter being carried out at the top of the laboratory in which the operation is practised, so as to allow of the escape of any uncondensed fumes into the outer air. To each pound of metal is added a pound and a quarter of nitric acid, of about 1·32 specific gravity. This latter must be pure, and quite free from any hydrochloric acid, for, as the proper solvent for gold is a mixture of nitric and hydrochloric acids, of course such an impurity would tend to loss of gold. The parting acid is, therefore, always examined with a little argentic nitrate, and, if this cause cloudiness, it is in that state unfit for parting with.

The acid and alloy then having been introduced into the apparatus, the joints are luted or made fast, and heat applied, cautiously at first, then, as the silver becomes dissolved out, the heat may be raised, for if this were too great at first, the action would be most violent, as the materials themselves generate much heat during the first solution of so large a mass of silver.

When action is ceasing, the liquid contents of the digester are removed, and fresh acid put on; a second boiling then serves to render the gold as fine as it can be made by these means. It is, therefore, removed after this, washed, and the solution of argentic nitrate set aside for reduction. This is best done by precipitation as chloride and the iron process; but in refineries it is very commonly reduced by plunging in plates of copper, which precipitate the silver at once, cupric nitrate being formed, which is then sold as 'blue liquor.'

The use of sulphuric acid for the operation is preferred at many refineries, particularly on the Continent. It is more economical, for not only is the acid itself much cheaper, but the resulting gold is more thoroughly freed from silver; indeed, it is said that gold which has been refined by nitric acid may subsequently have more silver separated from it by the sulphuric acid process. In operating the metals are so mixed as that the gold amounts to not quite half the weight of the silver. Pettenkofer, who has well studied this operation, says that 1·75 part of silver is the smallest working proportion of the latter metal; but in order that the mixture may be most fully acted upon it should not contain much more than 20 per cent of gold; and if it contain copper (which in small proportion facilitates the operation), this should be under 10 per cent, for if too much copper be present, a large quantity of cupric sulphate will be formed, which latter is insoluble in the strong acid liquors.

The alloy having been granulated, is introduced into a digester, with about 2½ times its weight of concentrated sulphuric acid. If a platinum digester is used, about 80 lbs. of alloy may be operated upon at a time. This is now boiled, during which strong action is evidenced by copious disengagement of sulphurous anhydride, while the silver and copper are simultaneously converted into sulphates. This first boiling is continued as long as sulphurous anhydride is evolved, which will commonly go on for about four hours. This gas, if allowed to escape, is very noxious, and is therefore better collected. This is often done, and it is reconverted by requisite chemical treatment into sulphuric acid. For the condensation of escaping products from the digesters, a large leaden chamber is usually employed; this is connected with them by a long condensing tube, also of lead, for, in addition to sulphurous, some undecomposed sulphuric acid always distils over; and a little argentic sulphate is generally carried over mechanically. The liquor is then removed, and a smaller quantity of acid again put on, the boiling being further carried on for a short time; after which the digester is allowed to remain at rest, in order that the gold may subside. For this second boiling, acid is often employed which has been recovered during other parts of the process. The liquor is next poured off and diluted. Repeated washing of the gold with boiling water is now necessary, for argentic sulphate is a very insoluble salt, and cupric sulphate when contained in so acid a menstruum, is also somewhat so. Hence, without such washing, the gold would be liable to be contaminated with the very alloys separated by the process. And again, the dilution effected in the silver solution, and consequently in the copper, during reduction of the silver, is advantageous, as this reduction progresses very slowly if the cupric sulphate formed be very concentrated; indeed, where such is the case, there is a tendency to reoxidation of the newly-precipitated silver.

The large digesters used in extensive refineries are now commonly of iron, in place of platinum, and the work is consequently carried out upon larger quantities, a quarter to half a ton of metal in ingots being worked at each operation. The strong acid used is inactive on the iron, which latter appears to leave its surface somewhat coated with silver, which is reduced upon it; and a smaller quantity of acid serves in an iron digester.

After washing the gold as above, it is again boiled in sulphuric acid, in a platinum vessel, and is next ready for melting into ingots.

The silver is recovered from the sulphate solutions by copper. The liquid is first drawn off into copper vessels, and heated up by steam. Plates of copper are put in, when the silver is precipitated in more or less of a crystalline state; and the operation is considered complete when sodic chloride ceases to precipitate anything from the solution. The silver crystals are then separated, well washed, and pressed, to squeeze the water entirely out; after which the metal is melted into bars. It is nearly pure, retaining only very slight traces of gold and of copper.

There are certain metals, as lead and tin, which require to be separated before employing these parting operations. This is to be done, in the case of the first, by cupelling the alloy, and in the second, by fusing it with nitre; otherwise, where platinum digesters are used, they would be injured by their presence.

Such are the principles of the methods of refining by acid, the actual practice being slightly modified in different refineries. As to the results, it may be stated that, operating in both cases upon large quantities, the nitric-acid process will afford gold of 993 up at times to 997 parts in the 1000; while sulphuric acid will refine up to 993, and rising from that to 998, and very frequently to 999 thousandths. But with great care the nitric-acid process may be made to produce as fine gold as the sulphuric.

F. B. Miller has described a method of refining in the dry way,[*] in a paper upon the 'Application of Chlorine Gas to the toughening and refining of Gold.' It is effected by simply passing the gas through the gold while the latter is in fusion. Thus several associated metals are converted into volatile chlorides, which escape. The silver is at the same time chlorinated, and may be separated as argentic chloride. After which the refined gold is remelted, and cast into ingots; and should any gold combine with chlorine, it is at once again decomposed; for gold parts with chlorine at about 420° F. = 216° C.

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[*] *Journal Chem. Soc.* vol. xxi. page 506.

Miller states that he was led to think of the chlorine process from the fact that mercuric chloride (corrosive sublimate) was used for toughening brittle gold; and as this acts by affording chlorine to the metals which induce the brittleness, it occurred to him to try chlorine itself.

It is no doubt true that mercuric chloride has thus been used, simply because, at the high temperature of melting gold, it at once parts with its chlorine; while the mercury itself, being volatile, is at the same time driven off. But it is a very expensive salt for the purpose; and not only is the mercury lost, but it at the same time carries with it a notable quantity of gold, causing additional loss.

In employing chlorine itself, it is of course an object to recover all the silver separated by it; but as the operation has to be performed in a clay crucible, and these crucibles are very absorbent, a large quantity of argentic chloride would, in its fluid state, not only be absorbed, but actually pass through and be lost, unless some means are used to prevent this. Again, as it is volatile, some would from that cause be also lost. Miller, however, finds that borax is of much use in both cases; for, by covering the melting material with borax in fusion, volatilization is almost stopped; while, by soaking the melting-pots in a saturated solution of the same salt, the pores become so filled as to prevent the absorption of argentic chloride entirely.

Plumbago crucibles cannot be employed, as they exercise a reducing action upon the argentic chloride, and, he says, 'probably from a small quantity of hydrogen contained in their material.' And, indeed, in many similar cases they cannot be used, from the reducing power of the graphite itself, so largely employed in their composition.

An ordinary clay crucible, then, is covered with a closely-fitting lid; in this a hole is drilled, to admit of the passage of a clay pipe for the conveyance of the gas to the bottom of the pot, and thus through the mass of melted metal contained in it. The outer end of this pipe is connected by a flexible tube with a vessel arranged for the evolution of chlorine, and the latter is fitted with a long safety-tube. In operating, after the air is driven out of the apparatus, the clay pipe is passed with the gas into the pot of melted metal. The gas passes quickly through it, and appears to be as quickly absorbed as generated. When orange fumes begin to be evolved, the refining may be considered as complete; and now—because, if the operation be prolonged, the gold itself may be attacked—the pot should be removed from the fire; and as soon as the gold has set, which will be in about 10 minutes, if in any considerable quantity, the still liquid chlorides are poured off, leaving the metal, as also the viscid borax, which will adhere to the pot. The argentic chloride is cast in a mould into a flat slab.

The gold is next remelted into bars; after which the silver is separated from the chloride by putting the cake between two plates of wrought-iron, and then plunging the whole into a vessel of water acidulated with sulphuric acid, when, after about 24 hours, the silver will be all reduced. It contains, however, a little gold; and if it is desired to separate this entirely, either the metal must be dissolved in nitric acid, and the silver solution poured off from the gold, and subsequently thrown down by sodic chloride, and again reduced in the usual way; or the metal must be treated by a plan also devised by Miller. He fuses the argentic chloride, and adds a little potassic carbonate to it, in order to reduce a little silver from it. This metallic silver, in subsiding through the argentic chloride, reduces any gold in its passage down (for it is probable that this gold was in chemical combination with some silver and chlorine), and alloys with it. The chloride is next poured off the little button which subsides, and which is composed of the gold, the reduced silver, and some adherent argentic chloride; the latter is decomposed by fusing the button with a little more potassic carbonate. Lastly, the poured-off argentic chloride is reduced as at first described, and will now be found freed from gold.

Miller says, 'One cubic foot of chlorine will theoretically convert eight and a quarter ounces of silver into argentic chloride; not more than twice this quantity is actually required in practice, and probably less. Thus, in refining 1000 oz. of gold, containing 5 per cent, or 50 oz. of silver, six cubic feet of chlorine would be theoretically required, and practically twelve cubic feet are amply sufficient; and this waste six feet is not all vomited forth from the chimney at once, but is gradually evolved during several hours. It can be readily intercepted in a small chamber furnished with a trickling stream of milk of lime.'

A late pupil of the author's, Mr. F. Smith, has been for some time working this process for one of the New Zealand Banks, and writing at the end of 1869, says that it is perfectly successful, and that his own impression is, that even for refining upon the large scale, it will much supersede the wet process, being cheaper and much quicker. He states the cost of operating in New Zealand as averaging twopence per ounce, and that it takes about two hours to part 300 ounces in one furnace. Their apparatus is very simple, and they employ white French crucibles.

In the year 1856 the coining operations of our Mint were much impeded by the importation of brittle gold, and various specimens were then referred to the author for examination by the Governor of the Bank of England, and the Master of the Mint conjointly, and since that date they have from time to time been troubled with the same brittleness. Hence, in 1869, according to the late Report of the Deputy Master of the Mint, Miller's process has been adopted for toughening such metal, and it appears with complete success.

Much American gold, both in coin and also in refined bars, made from Californian gold, is yet found to contain a native alloy of osmium and iridium, often in hard grains or flat scales. This is very injurious in working it, and especially for coining; hence it requires to be refined from it. Although the alloy is very infusible, and its specific gravity is as high as 21·1, it nevertheless cannot be separated from the fused metal by subsidence. The only dry method is to alloy largely with silver, viz. in the proportion of about 3 of silver to 1, so as to lower the specific gravity of the melted metal considerably; then, by fusing and allowing time for subsidence, while still in a fluid state, the gold and silver alloy may be nearly all poured or ladled off the iridium alloy. Fresh silver is then melted with this residue, and the same course followed several times until nearly all the gold is removed. The last residue is acted on by sulphuric acid to dissolve its silver, when the iridium and some pulverulent gold will be left, and these may be mechanically separated by washing as the gold is quite pulverulent, while the iridium is granular.

Iridium may, however, be separated from gold in the wet way, and Mr. Ridsdale, Chief Assayer at our Mint, has by long practice found the following to be an excellent and effective method of separating iridium from gold in the case of a singular alloy of gold, iridium, and copper, which is found to accumulate at the bottoms of the melting-pots during a long coinage of gold. The alloy is melted with three times its weight of silver, stirred well, and then granulated by pouring the contents of the crucible into cold water, stirring all the time whilst pouring. The granulated metal is then treated with hot nitric acid which extracts all the silver and copper, leaving the gold and iridium behind in a condition in which the former is readily dissolved away from the iridium by nitro-hydrochloric acid. The iridium remaining behind is washed and dried; the gold is recovered from its solution by either oxalic or sulphurous acid, and the silver also recovered from the nitrate solution in the usual way.

It will be seen, then, that these processes do not yield really fine gold, and it can only be obtained in perfect purity by dissolving the gold itself, separating other metals, and afterwards precipitating the pure gold again in the metallic condition.

The best material to operate on is ordinary refined gold.

This is to be dissolved in aqua regia, or acid composed of two volumes of hydrochloric, with one volume of nitric acid. The hydrochloric acid may have a specific gravity of about 1·16, and the nitric that of 1·45. The action of this upon the metal will be tolerably energetic; hence at first it is unnecessary to apply heat, but, as the action slackens, a moderate heat may be used. Each ounce of gold will require practically about 3½ ounces of mixed acid for its solution. When dissolved, it will be found that the silver has all been converted into chloride by the hydrochloric acid, and the greater part of this remains as an insoluble residue, although a portion will be held in solution by the strongly acid liquor. The solution is now to be poured into a porcelain basin, leaving the argentic chloride in the flask, and the basin heated, so as to evaporate the solution. When about one-third is evaporated, more argentic chloride will be found to have separated by the heat. It is well, therefore, to transfer the solution at this stage from this into a fresh basin, and evaporate as before. As the bulk reduces, small quantities of hydrochloric acid are to be added from time to time, which have the effect of liberating nitrous acid, by decomposing the nitric remaining in the liquid; but these additions must be very cautiously made, for the action produced is very energetic, and without due precaution, considerable portions of the now rich liquid will be spurted out of the basin. When the liquid has become of a deep ruby colour, and of the consistence of thick syrup, it is to be withdrawn from the heat, and allowed to rest for a time, when the whole of the auric chloride will crystallize, forming a mass of prismatic crystals. A pound or so of distilled water to each ounce of gold is now to be acidulated by a few drops of hydrochloric acid, and the mass dissolved in this; and it is better to allow this solution to stand a day or so, for argentic chloride, which is soluble in a strong acid solution, is separated by this dilution; therefore, by allowing this rest, it will completely separate and subside in the vessel; but the solution requires filtering, when it will pass as a brilliantly clear yellow liquid, and is then in a fit state for precipitation.

tolerably compact sheet or foil, or, lastly, in a spong
And these states may be attained with somewhat
although the circumstances determining the more co
are hardly yet well understood. It is commonly redu
trichloride just described. If this solution has been car
rated so as to be as neutral as possible, and especial
from nitric acid; a slight reduction of metal will take p
sure of the diluted solution to air, and the surface and
containing vessel will be covered with a deposit of
in all probability by the action of atmospheric nitro
face being more or less covered with delicate spang
standing any great length of time, precipitation will
place to a very considerable amount. Again, on add
water to such a gold solution, slight reduction of
duced, hence in diluting the trichloride solution b
latter should always be first acidulated with a little
acid.

Many elementary substances will precipitate g
trichloride. Thus sulphur or selenium, if immersed
tion, becomes penetrated by films of gold. A stick o
similarly placed in it, will speedily be coated with a fil
gold. Carbon also is effective, and Percy has some
reductions which he has produced on sticks of charc
the gaseous compounds of hydrogen are reducers
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similarly, but more slowly. In all these cases the brown powder is more or less interspersed with minute bright films, and at times with crystals. It may also be reduced by the battery upon a platinum pole in the form of a soft, brown nodular deposit, whose interior will be partly crystalline; and by the same means, from the double chloride of gold and sodium, but from this in a more arborescent and crystalline condition. Some metallic salts throw it down. Thus, trichloride of antimony (antimonious chloride) reduces it as a dull powder; but, when the solution of the metal is very concentrated, it falls in an arborescent form, it may, however, in the former state be contaminated with antimonic acid, as salts of antimony are decomposed in the presence of water. The arsenious chloride obtained by solution of arsenious acid in hydrochloric acid acts similarly on a neutral solution. It should be warm. In the case of the antimonial salt the formula would be, $3\ Sb\,Cl_3 + 2\ Au\,Cl_3 = 3\ Sb\,Cl_5 + 2\ Au$. The gold in these cases should be well washed with dilute hydrochloric acid, and when melted, fluxed with potassic nitrate, and borax. But considering the extremely injurious effects of arsenic or antimony upon gold, these precipitants are hardly safe ones. Mercurous nitrate throws it down in a very finely divided state, and hence in the form of a dark blue powder. Many organic bodies readily precipitate gold from the trichloride. Indeed, almost all will do so if a little alkali, as potassa, be first added, and the solution be heated on adding the precipitant. In some few cases the precipitate by organic bodies is not metallic gold, but an oxide combined with some of the precipitant. Gold is reduced from its solutions on coming in contact with the skin, linen, paper, silk, &c., and when acted on by light the stains produced become of a deep and permanent purple colour. Gallic acid, when added to a dilute acid solution, throws it down in the metallic state, producing at first a yellow solution, which afterwards soon becomes brown.

Potassic tartrate, citrate, or acetate, will each precipitate it; and sodic tartrate, which does not act upon a cold solution, will precipitate the gold suddenly, when heated. But the action of the salts of these vegetable acids will be retarded, if not prevented, by the presence of hydrochloric acid in excess.

The above are instanced as examples of the many classes of bodies which will precipitate the metal. Some of them, however, are uncertain in their action. But the three best precipitants may now be described: these are, oxalic acid, sulphurous acid, and ferrous sulphate. Of these the first is perhaps the best, although its action is slow and gradual; but it will afford gold of several textures, from a spongy mass up to a crystalline leafy precipitate or formation. A slight excess is to be employed, and the mixture of trichloride and acid to be slightly heated: indeed all these precipitants are much assisted by heat, but with oxalic acid heat is essential. Soon after its addition copious evolution of bubbles of gas takes place, and at the same time the body of the liquid appears filled with the most delicate spangles of metallic gold, which become coherent, and, under varied circumstances, may take any one of the forms just mentioned. The following equation will show the change:—$2\ Au\ Cl_3 + 3\ H_2\ C_2\ O_4 = 6\ Hcl + 6\ C\ O_2 + 2\ Au$. Here the oxalic acid parts with its hydrogen, which, by taking the chlorine of the gold salt and forming hydrochloric acid, sets the gold free, and the remaining elements of the acid decomposed escape as carbonic acid or anhydride.

The action of this precipitant being gradual, and capable of much regulation, by the amount and nature of the heat employed, while it is also peculiar in being attended throughout by this evolution of gas-bubbles which rise quickly through the solution, there is produced from the former cause a tendency in the metal to deposit in a crystalline or crystallo-granular state; while from the latter a more or less spongy character is given to it: hence it will readily be seen, that inasmuch as we are able to modify these conditions, so we can in the same degree influence the molecular nature of the result.

The final treatment required in the case of oxalic acid gold is simply to well wash it, and, if cast into an ingot, to fuse it with some hydropotassic sulphate, which will remove any argentic chloride, if such has been left in the solution; but this is not needed if the latter has been carefully separated, in which case the gold may be simply heated to dull redness, for oxalic acid is volatilized at a very moderate heat. Thus small quantities of gold may be welded into a mass without melting.

In employing sulphurous acid, a small quantity of potash may first be added, and then an excess of sulphurous acid; precipitation will immediately commence, and ultimately the whole of the gold be thrown down in a scaly, metallic powder, varying in cohesive quality — at times approaching that of oxalic acid gold. The action of this precipitant is very simple, and may be thus expressed: $2\,Au\,Cl_3 + 3\,H_2\,O + 3\,H_2\,S\,O_3 = 6\,H\,Cl + 3\,H_2\,S\,O_4 + 2\,Au$. Water is here decomposed, its hydrogen taking the chlorine of the gold salt. Hydrochloric acid is produced, the gold liberated, and, the oxygen of the water passing to the sulphurous acid, converts it into sulphuric. The after treatment of the gold may be the same as of that produced by oxalic acid, and already described.

In reducing by ferrous sulphate, a slight excess in solution is used. The gold is thrown down as an orange-brown powder. After all has subsided, the metal should be boiled in dilute hydrochloric acid, and this repeated two or three times, in order to remove all traces of iron compounds, which are apt to be retained by the gold. After the last acid, pure water is used; and the metal, when dried, may be melted with a flux of hydropotassic sulphate, in case, as before stated, any silver has been left as chloride in the solution.

Of ferrous sulphate in crystal, not less than four times the weight of the gold is required for complete precipitation. The reaction occurring is this: $2\,Au\,Cl_3 + 6\,Fe\,S\,O_4 = Fe_2\,Cl_6, + 2\,(Fe_2\,3\,S\,O_4) + 2\,Au$. Ferrous salts having great tendency to become ferric, the ferrous sulphate in this case readily parts with two atoms of iron to the chlorine of the gold salt, and forms with it ferric chloride: thus the gold is liberated, and the remaining elements of the iron salt are left in the condition of ferric sulphate.

Properties.—Gold has a perfectly characteristic colour—a most beautiful yellow, inclining to orange—and is susceptible of very high polish. Its specific gravity ranges from 19·2 to 19·5, according to its state. Pulverulent gold, or any of the forms of precipitated gold, are capable of being welded together, even when cold, by simple pressure and hammering; this pressure requires to be exercised moderately at first, and then the hammer used, in order to get solidity; otherwise a solid skin will be formed over the interior metal, which remains somewhat disintegrated. The author is in the habit of welding considerable quantities of gold precipitated by oxalic acid; and this is done in compact, solid masses, by heating them to dull redness in a platinum crucible, and hammering. The cakes of metal so made have all the texture of fused gold.

Precipitated gold may be mixed with silver, as reduced from chloride in the pulverulent state, and similarly compactly welded, affording a damasked cake of considerable solidity.

Gold is exceedingly ductile and tenacious, so that it may be drawn into very fine wire, one grain of metal drawing into 500 ft. of wire. These qualities may be assisted by its softness; for, when pure, it cuts almost like wax, exhibiting similar tenacity in cutting.

Of all metals it is the most malleable, and this property has been turned to account from the earliest knowledge of the metal. Thus a grain of gold may be extended over a surface 7½ inches square, and leaves of gold have been beaten to the 280,000th of an inch in thickness. In these, or thinner sheets, its transparency is well seen, when it will be found to transmit green rays. Faraday took a very thin film, and spread it upon a piece of glass; then, introducing between the glass and the gold a few drops of potassic cyanide in solution, as a 'cushion' for the metal, he spread it out, and by solution 'more attenuated it.' In this state it reflected yellow light, as ordinary metal; and, on looking through it, it transmitted green; but, on heating to about the temperature of boiling oil (viz. to about 600° F. = 315·5 C.), it lost its reflective power and green colour, and became translucent. When pressure was applied to such decoloured gold, by pressing with a hard body—a convex piece of rock crystal, for example—the green colour of the transmitted ray reappeared. (*Phil. Trans.* 1857.)

The precipitation of gold from its chloride by means of phosphorus has already been mentioned, and by this means Mr. Faraday formed some exceedingly attenuated films. He dissolved the trichloride equivalent to 1½ grains of metal in about 50 oz. of water, and then floated a few small particles of phosphorus upon the surface, using a perfectly clean glass vessel Thus the gold was reduced, and covered the surface with a continuous film, decreasing from the points of action (viz. the phosphorus) until so thin as to be scarcely visible either by transmitted or reflected light. The reflection from the thick parts was that of ordinary gold, although the films are porous. The colour of the transmitted light was grey, green, or dull violet, changing, on heating, to amethyst, and ruby, and assuming the peculiar green on the least touch with a card or the finger. A good method of observing the transparency of gold has been described already (page 8).

Gold may be artificially crystallized. If a small button of gold be fused, and then very slowly cooled, and subsequently treated with a very small quantity of aqua regia, solution will be commenced; but when the acid, by becoming expended and charged with auric chloride, nearly loses its power of solution, and this becomes feeble, it acts upon the mass of metal only in certain directions or lines, determined by the actual crystalline state of the metal below the surface. Thus the author has dissected out irregular groups of octohedra from such a button.

Gold is insoluble in either of the three ordinary mineral acids singly. It is, however, acted upon by selenic acid, if boiled in it. Its proper solvent is chlorine; and in dissolving in nitro-hydrochloric acid, solution is effected by means of the chlorine liberated from the hydrochloric acid, by agency of the nitric.

Patera states that an alloy of gold with silver may be dissolved in a solution of sodic chloride, if the solution be quite saturated with chlorine; and that such treatment will dissolve out the metals from ores equally readily. (*Osterr. Ztschr.* 1863, p. 165.)

Its fusing point is 2016° F. (=1102° C.); and it is doubtful if it is at all volatile *per se.* But if gold be alloyed with copper, it has been shown by Napier (*Quarterly Journal*, Chem. Soc. 1857) to be considerably volatilised, so that quantities, amounting to 4½ grains, could be collected during the pouring out of 30 pounds weight from a crucible. In regard to the loss of pure gold, described by the same author, the metal he employed was assay cornets, which will hereafter be shown to contain silver in notable proportion: hence the losses noted by him may have been due to this silver. The author has also shown (in a paper read at the Chemical Society, and published in the *Journal* for 1860) that mixtures of gold, silver, and lead, when cupelled together, volatilise considerably; and thus he collected considerable quantities of each metal from the chimney of an assay furnace after a few weeks' use only. Gold is an excellent conductor of heat, and also of electricity. Its atomic weight is 196·6; symbol Au.

The malleability of gold being so extreme, its extension into thin leaves is an easy operation, and the capability of beating gold must have been very early discovered; for in the description of the construction of Solomon's Temple there is a distinction made between things formed of 'pure' and 'perfect' gold and those 'overlaid' with fine gold.

It has commonly been stated that gold must be quite fine in order to beat well; but this is an error, for pure metal, in truth, requires more care in lamination. And again, as about a dozen shades of colour are sold, these are all got by varying the nature and quantity of alloy. Thus about 32 per cent copper will give a red gold. From 24 to 40 per cent of silver and 12 to 16 per cent copper give a variety of middle shades. Then, for pale colours or green shades, silver is added up to, and even beyond, equal weights. But when either copper or silver is used in any large quantity, it must be with gold alone, as addition of the two, except in small amount, injures the malleability of the alloy. The operation is thus carried on;—The metal is first melted at a good heat, with a little borax as flux, and cast in a very hot ingot-mould into small oblong ingots, of about 1½ inch long, ¾ wide, and $\frac{3}{16}$ thick, and weighing about 2 ounces each. The grease adherent from the mould, and any flux, are removed by heating them to redness; and this done, they are passed through a flatting-mill, furnished with very true rollers, and thus brought down to the $\frac{1}{800}$th of an inch (or thereabout) in thickness: this is effected by several rollings; and during the course of these, condensation of the metal is overcome by frequent annealing. After the last passage through the rollers and annealing, the ribbon is cut into portions of 1 inch square each, and these will be found to weigh about 6 grains in weight. These are inclosed between separate leaves of paper, and for this purpose the French gold-beaters use a very tough kind of paper which they manufacture for the purpose. The 'cutch,' as this case is called, is next wrapped up in a parchment double case, and is then ready for beating.

The anvil upon which this operation is performed is made of a dense black marble, fixed solidly, and where the support can be set in the ground it is better. As heavy a hammer as can be well wielded is used, and this is generally something over 15 avoirdupois pounds. Steady flat blows are delivered upon the cutch, the workman taking advantage of the resilience of the case in assisting him to raise the hammer after each blow. During the operation the left hand is employed in turning the cutch over and over, as well as round in different directions, so that any angular fall of the hammer, which would tend to produce unequal thickness of the sheets, may be counteracted; and the cohesion of them is prevented by occasionally bending the cutch backwards and forwards. Half-an-hour's work will thus bring the inch squares out to the margins of the cutch, that is, to a surface-measurement of 16 times the original one. These 4-inch leaves are then taken out, and each one cut into four; after which they are inclosed again, but now between sheets of fine gold-beater's skin, also incased in parchment; and as the beating becomes now a more laborious and careful operation, the weight of the hammer is diminished to 10 or 12 pounds. The extension to 4 square inches will now require nearly a couple of hours' beating; after which, if gilding-leaf is required, it is again beaten, and again with a smaller hammer: but it is these last operations which require great skill on the part of the workman, as well as fineness in the tools. The 'shoder,' as the gold-beater's skin case is called, must be formed of the picked membrane only; and even then, during the production of this very thin metal, many of the sheets will extend before others, and, reaching the edge of the shoder, be beat away, thus causing some irregularity in thickness in the different sheets. Vellum is sometimes used for cases.

The division of the sheets is at first made with a knife, but afterwards with a cross formed on a board by two sharp edges of cane, arranged so that the 4-inch sheet may be divided into 4 squares. This last division requires much dexterity, as does also the final cutting to size, and placing in books; for which purpose they are turned upon a leather-padded board by a pair of wooden pliers; and although a number may thus be heaped as it were together, a skilful operator will, by a tossing motion, assisting it by slight blowing by the mouth, thoroughly flatten them out for squaring. Lastly, they are stored in books of smooth paper, the leaves (for gilding metal) being often rubbed over with a little red ochre, to prevent adhesion.

Thus the original ingot of 2 ounces, and measuring superficially about ·6 of an inch by 1·5 inch, or a square of rather under $\frac{9}{10}$ths of an inch, is by the first or rolling operation brought at once to a surface of 180 square inches.

This, after the first beating in the cutch, is brought to 2880 square inches. Then after the second the 2880 become 11,520; and at the final one the measure will be 46,080 square inches, exclusive of small portions which by unequal extension are beaten off certain of the sheets.

These calculations show the 2 ounces of gold to have been been beaten into 320 square feet (not estimating any allowance for loss during the operation); but it is seldom carried so far as this, on account of the immense labour, and extreme thinness of the leaves, which would hence be porous, and capable of transmitting light. Therefore, an average of 200 feet to the 2 ounces may be assumed as the general workable thickness, and a leaf of such will be about one grain in weight.

For the operations of the Dentist quite fine gold is beaten, and in this case also sold in sheets containing 16 square inches of surface, that is, of four inches each way. In England these sheets weigh not less than 5 grains each; the medium 8, and the thickest 12. In America five thicknesses used to be made, viz. of 4, 5, 6, 8, and 10 grains per sheet. But now very thick is also at times employed, viz. rising gradually up to 480 grains, or 1 oz. per sheet.

The ordinary operation by hand involves rather hard labour, considering the weight of the hammer used, and hence machinery has been made in some places for the purpose, the hammer being worked by steam. And there is no reason why such should not with advantage supersede the old and laborious operation of hand beating.

Compounds of Gold. — *Oxides.* Gold has a very feeble affinity for oxygen, so that, although when ignited in oxygen gas it is dissipated in the form of a purple powder, this powder is merely finely divided gold and not an oxide. There are, however, two oxides, a suboxide (aurous oxide) and a sesquioxide (or auric); this latter has also feeble acid properties when hydrated, and forms a small class of salts called aurates.

Aurous oxide is formed by treating aurous chloride with a dilute and cold solution of potassa; but the potassa must not be in excess, or the precipitate it produces will be redissolved; also by precipitating aqueous auric chloride with a solution of mercurous nitrate; this latter must also be somewhat minus, or calomel would be precipitated; it falls as a dark-green powder, permanent at ordinary temperatures. Digestion in caustic potass converts it into a mixture of auric oxide and metallic gold. Hydrochloric acid will convert it also into metallic gold and auric chloride. It does not combine directly with acids. From its ready suspension in water it passes the pores of a filter, but the addition of a small quantity of potassic acetate and boiling will precipitate it. Composition, Au. 2 O; atomic weight, 409·2.

Au_2O.

Auric Oxide. — Auric chloride is prepared free from any excess of hydrochloric acid; this is then heated with an excess of magnesia, or of zincic oxide, either of which throws down nearly all the gold as oxide; but as it is more or less contaminated by the precipitant, it requires digestion in dilute nitric acid, which will dissolve any excess of the latter, leaving the oxide of gold unchanged. If the acid be strong, some gold will be taken up, but the addition of water will reprecipitate it. In the former case the oxide is yellow, and contains water; where, however, a strong acid is employed to cleanse it, it is brown and anhydrous.

Oberkampf advises the use of potassa for the preparation of this oxide; and accordingly, to a hot, neutral solution of auric chloride, he adds an excess of potassa, but auric oxide combines with alkalies, acting with them the part of an acid, as already stated. Hence, although this method is commonly mentioned as a good one, it is one in which an uncertain amount of product is afforded dependent upon this cause.

The hydrated oxide, when heated to 212° F. (= 100° C.), will become anhydrous; and if the heat be carried up to about 480° F. (= 249° C.), the oxygen is driven off and metallic gold left. It is soluble in strong sulphuric acid, but separates unchanged (as with nitric) on the addition of water. In hydrochloric acid it is converted into trichloride, and the action of hydriodic, or hydrobromic acids, is the same, the results being a corresponding iodide, or bromide of gold. If digested in ammonia it is converted into a deep olive-coloured compound, which is fulminating gold. Composition, $Au_2 O_3$; atomic weight, 441·2.

Aurous chloride is obtained by heating the crystallized auric chloride in a porcelain basin to about 347° F. (= 175° C.). This must be done in a sand-bath, and the mass be kept constantly stirred. A yellowish white mass is thus obtained, which, if the heat were carried to 392° F. (= 200° C.), would be resolved into metallic gold and chlorine gas; boiling water will convert it into trichloride and metallic gold. It is almost insoluble in cold water. Composition, Au Cl.; atomic weight, 232·1.

Auric chloride, or trichloride, is probably the most important binary compound, being the source whence other preparations of gold are obtained. It is made by heating gold into nitro-hydrochloric acid (as already described at page 253). We add to each atom of gold 1 atom of nitric, and 3 of hydrochloric acid. The evaporating temperature should not exceed 280° F. (= 138° C.), if it is above that, portions of aurous chloride will be formed. The crystals usually obtained mass together, and are very deliquescent; they are ruby red in colour: but if the ordinary solution be made, and care used to ensure excess of gold and hydrochloric acid, the nitric will all be decomposed, and from such a solution long yellow four-sided prisms and truncated octohedra may be obtained. These are very deliquescent, but not so soluble as the ordinary trichloride, they give a reddish-yellow solution, which is immediately rendered paler by the addition of hydrochloric acid. Berzelius says, that a perfectly normal solution of auric chloride containing *no* free acid can only be obtained by boiling aurous chloride in water. Thus, after getting a cake of auric chloride, it must be heated to 347° F. (= 175° C.), and then digested in boiling water, and filtered; but even then the solution will redden litmus. Composition, $Au\ Cl._3$; atomic weight, 303·1.

There are iodides corresponding to these chlorides, and formed by adding potassic iodide to aurous chloride or to auric chloride. In the first case a yellowish crystalline powder will be thrown down which is aurous iodide; in the second, a dark-green precipitate of auric iodide.

Berzelius describes an aurous sulphide as got by passing dihydric sulphide through a boiling solution of auric chloride, but Levol states that it is not a sulphide, but metallic gold. Also, that when dihydric sulphide is passed into a cold solution of auric chloride the brownish black precipitate is a compound sulphide formed of $Au_2\ S + Au_2\ S_3$. The same sulphide is thrown down on adding either ammonium or potassium sulphides to a cold solution of gold; but the precipitate is soluble in excess of an alkaline sulphide, a sulphur salt of the gold being formed, containing the alkaline sulphide as a base, united with sulphide of gold as an acid.

This sulphide of gold is resolved into metallic gold by heating, the sulphur being driven off at a dull red heat; or if the precipitate be left a few days in the solution whence it has been thrown down, its sulphur will be partly oxidized, and much of the gold is set free.

There is a somewhat curious compound of gold and tin, known as the purple of Cassius, which is much used as a colouring material. With porcelain it will afford various shades, from flesh-colour to deep red. Indeed, the ruby tint of Bohemian glass is due to this body. It has been supposed to be a mixture of metallic gold with hydrated peroxide of tin, but it is, as Berzelius assumes, more probably a hydrated double stannate of the oxides of gold and tin. It may be made by mixing one part of gold with 25 of tin, and 500 of silver (or zinc), and subsequently oxidizing this alloy by means of dilute nitric acid, which will dissolve out all but the compound sought.

But the best method consists in acting upon a solution of auric chloride by a mixture of stannous and stannic chlorides; the conditions required to produce the best result being that the gold solution be as neutral as possible, and that the chlorides of tin be proportioned very carefully (by experiment at the time of making the compound), so that, in truth, a sesquichloride may be formed, a step requiring some precaution, for the chlorides of tin as usually made are somewhat uncertain in their composition.

I have much used the following formula which yields an excellent result:—To ordinary dilute solution of ferric chloride, that is, such as would be of a colour resembling sherry wine, add solution of stannous chloride until the former loses its yellow colour, and becomes green. This is an evidence that it has parted with the quantity of chlorine sufficient to convert the stannous chloride into sesquichloride; the iron salt becoming ferrous chloride. This solution is then to be diluted with its own bulk of water. Next a solution of auric chloride having been prepared, as neutral as possible, and in the proportion of one part of gold in 360 of water, the tin salt is added with constant stirring as long as any precipitate is produced. This latter is to be washed as quickly as possible by decantation, and dried at a gentle heat. The iron salt does not affect the result.

Buisson* has published a method as follows:—A neutral solution is made of one part of tin in nitric acid; this is his first solution. Two parts of tin are then dissolved in cold nitrohydrochloric acid, formed by mixing one part of hydrochloric with three parts of nitric acid; a little heat may be cautiously applied towards the end of the solution, so as to ensure no stannous oxide remaining in the solution, and thus it will not precipitate the gold solution. This is called No. 2 solution.

Next, an acid of six parts of hydrochloric to one of nitric is made, and in this seven parts of gold are dissolved, and the solution at once thrown into 3500 parts of water; the whole of the solution No. 2 is then added to the solution of gold, and subsequently No. 1 dropped in also, but by degrees, ceasing directly the right colour is arrived at. If too little of No. 1 be used the colour will be violet, if too much it will be brown. If the precipitate does not settle at once Buisson advises the whole to be poured into a vessel of water in such a way as that they mix very gradually. When the powder has completely separated it is to be washed very quickly and dried.

As a proof of the uncertain composition of the purple of Cassius it may be stated, that published analyses range between 24 of gold to 76 of tin, and 78 of gold to 20 of tin.

In the moist state it is a reddish-purple powder, passing through various shades to brown, according to its preparation. When dry it always appears brown. It is soluble, while yet moist, in ammonia, affording a liquid of a purple red, and very intense in colour. From this solution it is again precipitated by acids, and it may also be recovered from its solution in ammonia, by simple evaporation. Hydrochloric acid has no action upon it, but boiling nitric, or sulphuric acid, brightens its colour, and dissolves out oxide of tin.

Alloys.—Gold and mercury combine at any temperature, but for the speedy formation of an amalgam, the gold may be heated; and added to the mercury, also slightly heated; but, if the gold be in a state of more or less fine division, it is soluble in mercury when cold. Gmelin states that an amalgam of 6 of mercury to 1 of gold crystallizes in four-sided prisms, and that the mercury may be distilled off from this, leaving the gold in an arborescent form. A bar of gold placed in mercury will become covered with small crystals, after about a month's immersion, the mercury penetrating the texture of the gold without destroying its malleability.

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* *Journal Pharm.* 14, 629.

The practice of 'water-gilding,' which was generally used before the process of electro-gilding was known, depends entirely upon the capability of amalgamating gold with mercury. The article to be gilt is covered with such an amalgam, the mercury then driven off by heat, and the gold finally burnished on.

The operation is this. Six parts of mercury are heated with one of gold, and the resulting amalgam squeezed, so as to separate superfluous mercury. Thus nearly four of the six parts of mercury will be squeezed out, and a mass of the consistence of butter left. The object to be gilt is rubbed over with a solution of mercurous nitrate: thus it becomes covered with a superficial layer of that metal. And now the amalgam is applied, and will at once attach itself to the mercurial surface. It is then washed, and gently heated over some burning charcoal, and the amalgam kept uniformly brushed over the surface by means of a soft brush. The heat is then kept up, until the surface assumes a dull yellow colour, when it is removed, and polished by a wheel brush, kept moist by dilute vinegar. A mixture of bees' wax and verdigris is then applied, the latter having an affinity for mercury, removes any which is still left on. Lastly, the article is burnished, washed with dilute nitric acid, and afterwards with water, and dried. The whole operation however is most noxious to the health of those who practise it; hence electro-gilding has almost superseded it.

Gold and silver unite in any proportion, affording alloys of all tints of colour between silver and gold, such being white, greenish white, green, greenish yellow, up to the orange yellow of gold. When alloyed in equal proportions all colour of gold is lost, the alloy being nearly as white as silver. Three parts of silver to seven of gold gives a green alloy. By adding silver the hardness of gold is somewhat increased, without at all diminishing its malleability. It is rendered rather more fusible. No gold is found in nature without silver, and, on the other hand, no silver is free from traces of gold, even refining will not entirely separate silver from gold, and it is only to be done by the laboratory operations for pure gold already described.

Platinum alone, is not very hurtful to gold, but a mere trace of palladium with gold, will render the latter very brittle, and gold ingots are sometimes met with, into the composition of which palladium has found its way. And it is further troublesome, because not very readily separable by refining operations, and the same may be said of platinum as to refining. The latter metal is sometimes mixed with gold, for the specific gravity of the gold is not diminished by this alloying, and again its presence may be overlooked by want of care in assaying (this will be spoken of in the assay of gold), while at the same time its commercial value is so much below that of gold, that it becomes a very convenient agent in the hands of the fraudulent.

The metal iridium is frequently met with in gold as already mentioned (p. 252) not alloyed, but merely disseminated throughout the bars.

Gold and copper form a reddish alloy, very much harder than either of the constituents, the maximum hardness being exhibited by an alloy of seven parts of gold with one of copper. If the copper be pure, the malleability of the gold is not much destroyed; but the least trace of antimony, arsenic, or lead, associated with the copper, will render the alloy completely brittle.

From the hindrance occasioned to coining operations by these metals, in 1856 the author was engaged as already stated (p. 13) by the Bank and Mint authorities to investigate the matter; for the question at issue was whether the bars as imported into the Mint by the Bank, contained the offending metals; or whether they were introduced in the alloy employed by the Mint, for they were all above standard value, and consequently had to be lowered by alloying. The copper therefore was analyzed, also a certain number of the gold bars which had been sent in. The copper was comparatively free from impurity, and the following analysis of the bar-gold before melting for alloying, gives a fair sample of the whole, and shows sufficient impurity, and of such nature as to account for the condition found at the Mint. Gold 98·68 per cent, silver ·83, iron ·42, separated antimony ·027, antimony with tin not separated ·043.

The total amount of antimony and tin here, viz., ·07 part (being 1 part in 1410 of alloy), is quite sufficient to confer the amount of brittleness which existed, and further, any trace of arsenic remaining in the copper would add to it in association with the above metals. Here however the copper was free. In such cases of analysis the argentic chloride should be examined for tin and antimony, some of which will go down with it by action of the nitric acid in the solution of the sample.

On witnessing the rolling and adjusting to thickness of the standard metal found from the above, it was seen to pull to pieces under the strain of the drawbench, and when a fillet was completed which it was almost impossible to do, it was unworkable in the coining press.

Gold, for purposes of coinage, would, if pure, be too soft to stand the hard wear to which coin is subject; hence it is always alloyed, either with a mixture of silver and copper, or with copper alone. This is the case with all gold articles required to maintain their shape. But in jewellery alloy is employed not only for hardening, but in some cases to modify colour, most frequently, however, to economise precious metal, and here of course alloying metals are proportioned so as to alter colour as little as possible. But where it is much injured, colour is restored by removing the surface-alloy by solution. Hence all 'coloured' articles have a surface of pure metal, and are too soft to wear well.

The best alloy for coinage purposes is equal parts of copper and silver. In this the extreme hardness which copper gives where used alone is modified, and the piece yields in wear in place of abrading as a hard alloy is apt to do.

This was the alloy of the old English guinea, a coin famous for resisting hard wear, and possessing at the same time an excellent colour. Our present coin is made regardless of the nature of the alloy, as they are now without the means of carrying on refining operations at the Mint; hence in a dozen sovereigns a practised eye can detect nearly as many shades of colour, dependent upon the amount of silver contained in the gold before alloying, having rendered more or less copper necessary. In the American coin the alloy is chiefly copper; thus the coins are of a red tint, and very hard.

Discrimination of Gold.— 1. Dihydric sulphide or ammoniohydric sulphide gives a brown precipitate of auric sulphide, but the second is never used as a precipitant as the resulting sulphide is soluble in it, as also in the sulphides of sodium or of potassium. The precipitate is insoluble in nitric or in hydrochloric acid separately; but soluble in aqua regia.

2. Ferrous sulphate is a most delicate test, producing a beautiful blue tint, even in exceedingly weak solutions.

3. The characteristic test is stannous chloride; and thus a gold salt, containing only $\frac{1}{50}$th of a grain of gold, dissolved in half a pint of water, will, with a few drops of this reagent, give a pale brown precipitate; this is deeper as the solution is stronger, becoming deep brown where the same quantity is dissolved in about 100 grains; and metallic tin is even more delicate in this reaction.

4. Mercurous nitrate reduces it as metallic gold, and as a dark brown precipitate.

5. Lastly, if the compound be a solid, heating will reduce it, and metallic gold will be left.

For the estimation of gold quantitatively, oxalic acid may be used to a solution containing a little excess of hydrochloric acid. The precipitated gold will, however, be some time in completely separating (not less than 24 hours), and the solution will require to be well heated. When all is precipitated, the gold must be collected, washed, and ignited at a low red heat, before weighing. By this any oxalic acid will be volatilized, supposing any be previously retained.

Ferrous sulphate may also be employed, and its action is somewhat quicker than that of oxalic acid. The precipitate here requires washing with a little dilute hydrochloric acid, and gently igniting, as in the former case, before weighing.

At times, where the separation of gold has to be made from some other metals, it may be precipitated by dihydric sulphide. But here, after washing, the precipitate is ignited, and the result weighed as metallic gold.

Gold may be separated from mercury in the wet way, by making a solution in nitro-hydrochloric acid in the usual way; then precipitating by oxalic acid. The precipitate is acted upon by some hydrochloric acid, so as to dissolve out oxalate of mercury. The gold is weighed after washing and igniting. Lastly, the mercury is separated by stannous chloride, and weighed (page 146).

Although somewhat in advance of the subject, the analysis of a portion of alloyed gold may be here considered, premising that the relative proportions of gold, silver, and copper, only are desired to be known. The alloy would be dissolved as usual, separated from argentic chloride; then evaporated, dissolved, and diluted. Thus the rest of the argentic chloride would be precipitated, and may be collected on a filter, with the portion left from the acid solution. This filter must be very thoroughly and quickly washed with water acidulated with a little nitro-hydrochloric acid, and subsequently with hot water, or it is apt to retain notable quantities of gold.

The silver is weighed and calculated as already described. Next throw down the gold quickly by oxalic acid, and heating. When all is down, heat the collected gold to redness in a platina capsule: this decomposes any other oxalates formed. After this the gold is to be boiled in hydrochloric acid, which dissolves any copper out; and if traces of iron, lead, or antimony be present, these will also be so removed.

The remaining solution may now have some ammonia added to it: this will retain the copper in solution while it precipitates other metals. These latter are to be filtered away, and the clear blue liquid treated with caustic potass, and boiled. The cupric oxide precipitated is to be filtered out, washed, dried, and the filter carefully burned after the separation of the precipitate, lest any oxide should be reduced to suboxide. The precipitate is, lastly, ignited and weighed. (See Estimation of Copper.)

Before treating of the actual assay of a specimen of alloyed gold, it will be well to examine the methods by which assays may be made of ores, quartz, &c., containing gold, as such latter must, in fact, be carried out in such cases, preliminary to the cupelling and parting operations used upon alloys.

Many such matters may be treated precisely in the way described for silver: thus they may be fused with litharge in a crucible, or they may be treated with lead, and scorified. In either case the button resulting is subsequently worked in the usual way, by cupellation, &c.

Suppose it be desired to estimate the amount of gold in a small specimen of quartz. In order to facilitate powdering, it may first be heated to redness, and plunged in a basin of cold water. This splits it into such small fragments as to render powdering easy in an ordinary mortar. From the powder, from two to five or six specimens may be weighed, of 300 grains each (more or less being taken according to presupposed richness), and the assays made from the number are averaged for the result. But where, instead of upon a small specimen, the operator has access to a quantity, something like a ton should be broken up and well mixed, and from this several quantities should be selected, the whole done with such plans and precautions as circumstances may suggest as likely to give a fair average of the whole, for much care must be exercised in order to ensure a sample giving a fair representation of the value of the bulk; and the more so from the value of the resulting metal, and also considering the fact that it is as often found diffused in isolated grains or filaments through the matrix as it is in a more regularly distributed condition. Any such grains separated during powdering and sifting may, of course, be at once removed and estimated.

Having weighed the portion of powdered ore, litharge, equal in weight to the sample, half the weight of dried sodic carbonate, and rather more than half of powdered charcoal, are next mixed with it, and the whole put into a black-lead crucible of such capacity as to be about half filled by it; a little borax is next sprinkled over all, and it is ready for the furnace.

It may be mentioned that the above are average proportions, which may be varied according to the presumed quality of the specimen.

The crucible is next heated in a Sefstrom's furnace, or in a small wind furnace, the heat being steadily raised; for, if too great at first, the effervescence caused by the escape of carbonic acid from the soda salt, which is produced by the silica taking its soda, would endanger loss. Moreover, this violent action is increased by the union of carbon with the oxygen of the litharge. When the action has become somewhat moderate, the heat may be urged to full redness, so as to render the mixture quite homogeneous. A double circular ingot-mould being provided, the crucible is removed, and the contents poured, the slag first, into one concavity. The pouring is stopped when the reduced metal is about flowing out; the latter is then to be poured into the other cup of the mould. When cold, they are taken out; and the button, being flattened to free it from any adherent slag, is ready for cupellation. The litharge is apt, without care, to permeate the crucible after effervescence is over. This must be prevented, or the result will be worthless. (See pages 102 and 106.)

Phillips* advises the use of litharge or red-lead alone, but with a small quantity of a reducing agent, viz. charcoal, and says that when the rock operated upon does not contain any appreciable quantity of iron pyrites, or any other metallic sulphide, 600 grains of finely-powdered ore is to be intimately mixed with 4000 of litharge or red-lead, and 15 to 20 of flour, starch, or finely-powdered charcoal; and he adopts this weight of ore as convenient, being such a one as is easily fused in a No. 10 French crucible. It is heated until in fusion, withdrawn, cooled, and the crucible broken; the button of rich lead is cleaned for cupellation.

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* *Mining and Metallurgy of Gold and Silver*, page 227.

A second example may be given in the treatment of auriferous pyrites, where, of course, much sulphur is present. Here, then, the first step after powdering is to roast the material well, so as to drive off the sulphur; and by this treatment the iron will simultaneously be converted into oxide. For this first step the powdered ore is put into a scorifier or a roasting dish, and placed in a muffle. The roasting should be begun at a very moderate temperature, and with frequent stirring; for if too great heat is used at first, the materials would fuse and cake; but as sulphur is evolved, the heat may be raised by placing the dish in hotter parts of the muffle.

A weighed quantity of this roasted ore may be next treated as detailed for an ordinary quartz specimen; but Phillips advises fluxes in the following proportion, viz. to every one part of roasted ore six parts of litharge, one of dry borax, and from 15 to 20 grains of charcoal, just as much of the reducing agent being needed as will give a button of lead sufficient to collect the whole of the gold, and a button of a convenient size for cupellation: too little lead would endanger loss of gold; too much would, on the other hand, give so large a button as to be troublesome in cupellation.

Assay of Gold Alloys.—In earlier days of these operations, when, for commercial purposes, they were not carried to the nicety of the present time, it was common to make a kind of rough assay by means of the touchstone, and, in experienced hands, with pretty good results, so that even now the plan is occasionally followed for small articles of jewellery and the like. The requisites for the process were a few needle-shaped pieces of gold, of various known qualities, commencing with one of fine gold, and passing down to 18 carat gold by half carats. Thus the first would be 24 carat, or fine, the second 23½, the third 23, and so on. Then, after 18 carat, descending in quality by a whole carat at a time.

The touchstone is a piece of hard basaltic stone, with a surface just rough enough to abrade the metal and retain a small portion of it upon its surface for examination by acid. The acid employed is nitric, of about 1·20 specific gravity. The sample to be examined has some angular part of it drawn across the surface of the stone; but, as in articles of jewellery, the surface is often what is termed 'coloured,' and consequently richer, a few rubs are given of the part to be examined upon some rough surface, previous to making the testing line upon the touchstone. The assayer then takes one or two needles which he supposes to be near in quality to the one sought. These are drawn across the stone, and then all the streaks are moistened with the nitric acid. If the quality of the unknown specimen is nearly the same as that of one of the needles used, the action of the acid will be nearly similar in the two; if not, the streak made by the coarser of them will be most acted upon, and his experience would then point out, by peculiarities in the test streak, what needle he would have to choose for final comparison. The action of the acid is upon the alloy, and gives a more or less green solution. The gold is untouched. The practice is, however, a very rude one, and at best depends too much upon judgment.

The outline of the operation for the actual assay of gold is as follows:—An assay pound of the alloy is first very accurately weighed; next, pure silver, to the amount of from two to three times the supposed weight of gold is added; then this is cupelled with a proper proportion of pure lead. The button so obtained is now flattened somewhat by the hammer, and then rolled into a ribbon. This ribbon is annealed and coiled, and is then ready for the parting operation, which consists in boiling it twice in nitric acid, and, between and also after the boilings, washing in water. Lastly, annealing the fine gold, and weighing. Gold (in assaying operations) is best weighed decimally. Thus, in a pound, or 1000 parts of English standard gold, we should find 916·66 of fine.

The decimal 6 may be carried out as it is a recurring one; and as, with proper care, assay results of gold may be easily brought to a tenth of a millieme, so reports may be well made to that degree of closeness. The decimal weights may be converted into trade by calculation, but there are now complete tables published for this purpose.

The system of trade weights for gold is not the pound divided into ounces and pennyweights, as for silver; but the pound, or 1000 parts, is said to contain 24 carats, each carat 4 carat grains, and these latter are divided into halves, quarters, and eighths; the eighth, or 768th part, thus equalling the decimal 1·3 (or a little over). Up to about twenty-five years since assay reports for the purchase of gold were only required up to the quarter of a carat grain. But about the year 1852 the Bank and Mint required them to be made to the eighth, and at the same time desired the decimal report to be sent in also; then, as in purchasing they paid to the eighth of a carat grain only, any small decimal above that of the nearest eighth was so much profit to the buyer. For example, supposing a bar was found by the assayer to have 917·6 per thousand of fine gold in its composition, he would report this decimal, but with it the trade report of standard, and the difference between 917·6 and 916·6 (the true value of standard) or one thousandth would be so much profit to the purchaser, for although better than standard, it could not, of course, be reported as better one eighth, unless the decimal was as high as 918·0.

The Bank have lately altered their plan of reports, and now require the decimal to the third of the millieme only.

As the assay pound is supposed to represent the troy pound of 5760 grains, the carat eighth will be just 7½ troy grains.

The actual weight of the assay pound may vary much according to the practice of the operator, thus some assayers (those who follow the French directions) use only 7·5 grains, the half gramme, while, on the other hand, English assayers will use from 10 up to 16 grains. The capability of using a tolerably large weight of course assists in the greater delicacy of the small weighings. By a trade report, as it is termed, standard gold, which contains 11 parts of gold to 1 of alloy, would be said to be 22 carat gold, any specimen containing more gold would be called 'better,' and less than that amount 'worse.' As this method of weighing is still used by many assayers, an illustration or two may be given. Having at first 'weighed in' an assay pound of metal, and carried it through the various stages of the operation, the fine piece of gold resulting is placed in the balance; in the other pan is put the 22 carat, or standard weight. Suppose the gold does not counterpoise this, sufficient weights are added upon the gold pan, and thus, supposing a carat grain, a half, and an eighth, were found necessary, the gold would be reported, W. 0 carat, 1⅝ gr. If, on the other hand, it was heavier than the standard weight, and weights (say) of 1 carat, 2⅝ gr. were required to be added to the weight pan, the report would then be, B, 1 carat, 2⅝ gr. Thus gold of 18 carats fine would be written, W. 4 carats.

The rough weights of metal for the gold assays being prepared by an assistant, are weighed in for the furnace by the assayer himself, as described in the silver operation (page 205), any small additions or deductions made, being done by cleanly snipping off minute pieces with snips, until the weight is very closely adjusted, when any slight deviation from zero of the balance may be noted to be allowed for 'in weighing out the assay.' The practice advised by some of reducing the weight by a file is very objectionable, as the file dust is sure to adhere to the hands, and thus lead to inaccurate weighing, being liable to fall into the balance pan or skiff in which the metal is weighed.

The operator then judging quality from external appearance, &c., next adds to the specimens of metal the requisite amount of pure (or 'water') silver, and then wraps silver and gold together in a piece of sheet lead, weighing half the amount of the lead required for cupellation.

The quantity of lead to be employed will be about 6 times the weight for gold down to about 920. Below that and down to 750, 8 times will suffice. And for qualities below the latter, 10 will often be required, although these proportions are often modified by the presumed nature of the alloy.

The furnace being prepared and heated just as described for silver, the assays are charged in when the heat is judged to be sufficient, and the cupel operation is then carried on, as with silver. But the care requisite here is very much less than that needed for silver assays, the object being as much the alloying of gold and silver, as the complete separation of oxidizable metals; because any small amount of the latter left in the assay will be removed by the acid in the parting operation, which retained alloy in a silver assay, where there is no after assisting operation would be just so much of error. A certain amount of care is, however, to be exercised for several other reasons; thus, for example, if assays, and especially gold ones, be charged into cupels insufficiently 'seasoned' (see page 192), 'spurting' is to sure result: this is the throwing up from the bath of fused metal of a number of small beads of the assay; these will be projected even to the crown of the muffle, and falling all around, spoil the assays in the surrounding cupels. Again, loss may accrue from vegetation or springing if the assays have been carelessly cooled down: and, lastly, a muffle not properly cleared, or having a fragment of coal shut up in it, will, by containing an atmosphere of carbonic acid, cause reduction of the oxide of lead at the external parts of the cupel, which reduced lead, being taken by the yet fluid button, will render it so brittle as to fly to pieces under the hammer.

The flatting hammer requires some dexterity in its use. The buttons being taken from the furnace are one by one placed upon an anvil and struck about three blows; the first, a downright one, gives the piece the diameter equal to the width required of the ribbon. The next blow is a kind of drawing one upon the edge, whereby a kind of tongue is drawn out sufficiently thin to cause it to be readily seized and drawn in between the rollers of the flatting-mill. The other end of the assay is then turned round, and a similar blow and conformation given to it.

The board containing the flattened buttons is now taken to the rolling-mill, and all are passed through, with the rollers set just at such distance apart as will equalise the assays. They are next adjusted down to the distance which shall elongate the assay into a ribbon of metal required; and now if the flattening operation with the hammer has been well performed, they should all be of equal breadth, and for an assay pound of 10 grains, should measure about ·4 of an inch wide, the rolling operation, bringing them to 2·2 inches long.

This treatment of the metal will, however, have rendered it very hard and dense, therefore annealing is required before the parting operation, for which purpose the assays are placed in a solidly made iron tray, each one in a separate division. The tray is put into the muffle and heated to dull redness, after which it is taken out and the ribbons of metal coiled up into small cylindrical rolls, called 'cornets.'

The requisite number of assay glasses are then each charged with from 2 to 3 ounces of nitric acid of a specific gravity of about 1·20. They are very readily charged by employing a pipette which contains the requisite quantity, and filling from a tall glass jar of acid, thus a set of 50 glasses may be done in a few minutes. The filled glasses are then arranged upon a gas parting apparatus. A small one is shown in fig. 59, and the method of condensing acid in such a small arrangement. It consists of a tube, A, connected with the gas supply. On the upper part of this are screwed a number of cocks; and on the outer screw of each of these a cup-shaped burner, B, is screwed; the jets of the burner, passing out horizontally from its circumference, cause the flame from each to wrap itself round the end of the glass. For a small set of from 6 to 12 burners the arrangement shown in the drawing may be adopted where the whole are fixed in a mahogany stand. This latter is furnished with a set of long tubes, D, one for each glass, C; and when the evolution of acid vapours commences these may be inserted in the necks of the glasses: thus condensation of the acid takes place in them, and the condensed product runs back into the glass, while the escape of noxious vapour is to some extent moderated. In an active laboratory, where 50 or often more are worked at a time, it is necessary to arrange the whole in some convenient chamber, provided with a flue for carrying the acid vapours away. The tubes D are then dispensed with, and the burners are better to be placed upon two or even three gas tubes, so as to render the apparatus more compact, and bring all the glasses well under the eye of the operator.* These burners

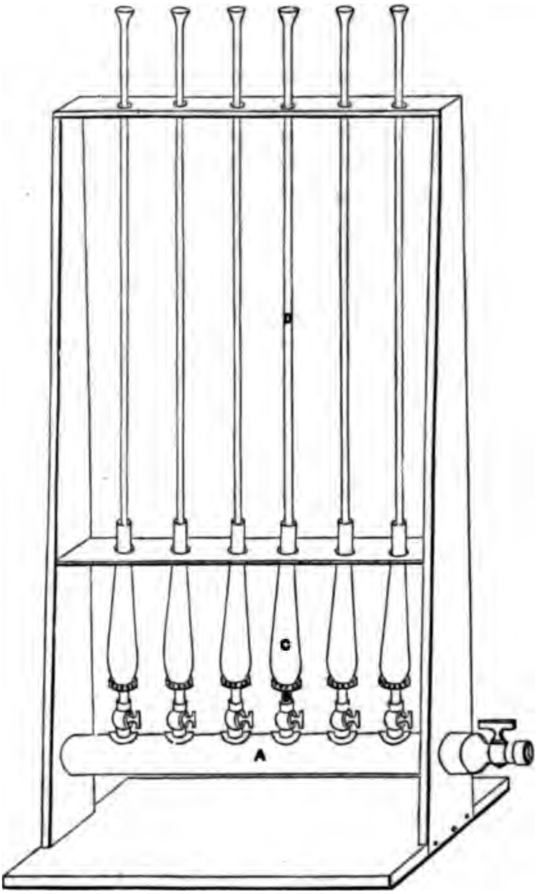

Fig. 59.

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* The condensing-tubes should be shouldered at their lower ends to prevent their passing too far into the assay flasks.

were first employed by Mr. Claudet in Professor Graham's laboratory, and subsequently in his own. I early used them, and for many years found them most efficient. In our Mint Mr. Field improved upon them by employing Bunsen burners: these are of great advantage, as there is no smoking of the glasses by them, although in the plain burner this is not often the case, as the gas is rarely burned much above a blue flame. In Field's apparatus he has an excellent plan for lifting the glasses off in rows.

After the assay glasses have cleared of red fumes, from 3 to 5 minutes' brisk boiling is kept up; they are then removed from the burners, and the solution of argentic nitrate poured off, the cornets washed with a little hot distilled water, and a fresh dose of acid put into each glass (now of a specific gravity of 1·3); they are then boiled again for 15 or 20 minutes, after which the acid is poured off and the glasses quite filled up with warm distilled water.

It will be found that acid of the above density is apt to boil unsteadily, and its vapours, by adhesion to the sides of the glass, will be given off irregularly and with such violence as even to project nearly the whole of the acid from the glass. Hence it is found necessary to put some body in with the assay, which, by affording points for the evolution of the vapour, shall facilitate its steady delivery from the fluid. For this purpose the practice by many is to use a piece of charcoal; but this is apt to induce the evolution of nitrous acid, which, by absorption in the acid, will even dissolve portions of the metal. This has been proved by the author, and put forward in a paper published by him.* Moreover, the acid becomes much discoloured by charcoal: hence Field has proposed the use of small balls of porous earthenware, and these answer the purpose most admirably.

If these acids are examined, it will be found that the first has removed nearly all the silver, viz. to within 5 per cent of the whole, which residue is very nearly separated by the denser second acid; the small quantity left being generally very nearly a constant quantity, varying with each assayer's practice.

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* *Quarterly Journal of the Chemical Society*, 1860.

The assays are next turned into small porous earthenware crucibles for annealing; but the cornets, with the silver now removed, occupy the same bulk as before parting: hence, from their spongy and consequent friable nature, much care is required in effecting this, or they are sure to break up. The pot is therefore first filled with water, and the neck of the glass stopped by the fore-finger; then, being dexterously inverted under the water of the pot, the finger is removed, and the assay allowed to fall steadily into the pot, time also being given for any pieces (if any should by chance have become detached) to fall on to the assay. In this operation, if the piece even touch the finger in its transfer, portions are very likely to be detached.

The pots are now arranged in the furnace, and heated up to an annealing heat. thus the former bulky cornet is condensed and shrunk considerably, while its surface, by incipient fusion, becomes perfectly metallic, changed from the brown lustreless appearance it had when washed off to a pure golden surface.

In 1854 Tookey and Henry* made some experiments upon boiling 'a batch of assays simultaneously,' and for this purpose they employed short tubes of glass, shouldered at one end so as to support them in a porcelain plate or tile. The bottom of each tube was closed by a circular piece of perforated platinum foil. They lowered this arrangement in a vessel of nitric acid, and boiled twice, 'washed, dried, and annealed,' managing the whole as one assay, and thereby saving a considerable amount of time.

An excellent, although costly apparatus, has been devised by Matthey, and used in his assay office, whereby the acid work, with the necessary washing and after annealing, are all carried out in the same apparatus, in which also they are then brought to the balance without removal, for weighing out. It is shown in fig. 60, where (*a a*) are boilers made in platinum and furnished with platinum covers and condensing tubes (*b b*) which convey the vaporised acid by a funnel into some fit vessel for condensation and collection (*c*); (*d*) is a platinum tray, divided to carry a number of platinum cups. These little thimble-like cups (fig. 61) are made with fine saw cuts through their bottom for free circulation of the boiling acid, and are arranged in rows in the tray.

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* *Journal Chem. Soc.* vol. viii. series 2, page 366.

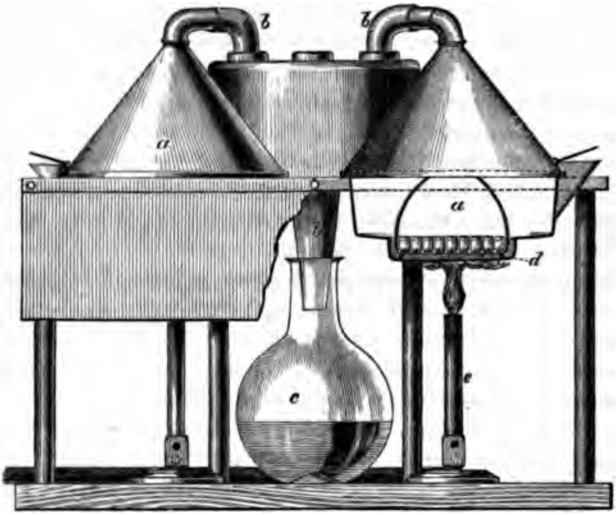

Fig. 60.

On coiling the annealed ribbons they are placed at once separately in these cups. The requisite quantity of acid being put into the boiler it is heated up by a Bunsen burner (*e*), and the tray is then lowered into the acid by the aid of a platinum hook. The right-hand boiler in the figure is shown in section with the cup tray lowered in it. In front of the left hand is a portion of a screen placed for protection of the burners from drafts of air. The cornets are then boiled the requisite time, after which the tray is removed, and, with its contents, well washed by immersion in boiling distilled water. It is then put into the boiling vessel a second time, and with stronger acid. After the second boiling the tray is again removed, and finally washed with hot distilled water, after which it is placed in the muffle

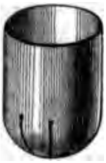

Fig. 61.

and a low annealing heat given it so as to render the cornets fit for handling and weighing. Care must be used here not to get the heat too high, or the cornets are liable to adhere firmly to the platinum cups. For platinum and gold weld very readily together. The assays are now ready for weighing out.

Matthey's apparatus was introduced into the Mint Assay Office by Mr. Field, the late resident assayer, and he has somewhat improved it by having a small well or depression formed at the bottom of the boiler, by which, when the tray contains only a few assays, they may be worked with a corresponding small quantity of acid. He has also had a pouring lip put to the boiler which is a convenience. It has been sent out for use in the New Mint now in work at Melbourne; and I have just received an account of its working from my friend, Mr. Barton, the Assayer to the Mint. He says, 'The apparatus of Matthey's is a very great success, and we like it much ;' and, again, 'The platinum apparatus is a great saving of time, and only requires one to attend to it, and the work is beautifully regular.' He has, however, very slightly altered its arrangement, and also his plan of boiling, in order to suit his office arrangements. The testimony of an operator who has had the experience of Mr. Barton is valuable and reliable.

The disadvantages of the apparatus are, perhaps, not to be mentioned when its usefulness is remembered. But the following are the chief. First, the tendency to adhesion between the fine spongy gold, and the platinum during the annealing operation. This causes any small pieces, if such are detached, to adhere rather readily, and very firmly, to the red hot cups.

Hence, it is necessary not to anneal so fully as when the old clay annealing pot is used. Then in a set of glasses any assays which may contain platinum or palladium are at once detected by the colours produced in the acid by these metals. Here, however, where the acid is used in bulk for a whole set of assays, any such individual cases, of course, escape entirely this means of detection. But Mr. Matthey constructed it more especially for assays of metal of known and uniform composition, as coinage bars, for example, and for such its advantages are very great.

After the acid work and annealing, it only remains to weigh the assays, but compensation must be made for a certain retention of silver; this not only varies with different operators, ranging from 1 to 10 grains in the pound, but is subject to slight difference, at times, with the same assayer, dependent upon variations in the furnace heat, atmospheric influence upon the boiling of the acids, and other disturbing actions. Beyond this there will be, on the other hand, a drawback, to be given from the previous deduction, this is for loss of gold during the operation, which is subject to like variation with the silver retention, and averages about 1 to 6 grains in the pound. Hence the operation can only be carried on to perfection by those who are continually practising it; and in such hands it needs daily tests to be passed with the working assays, as proofs or standards, whereupon to base the necessary corrections to be applied. Thus, in each large batch of assays, say of 50 cupels, two standards at least should be employed, one should be of perfectly pure gold. The second may well be of 916 parts of gold with 84 of copper, or the alloy may be made by 42 of copper with 42 of silver; constituting in either case near about standard metal if such were mixed; but here the quantities are weighed separately and folded together with the quartation silver in the lead case. From the working of these standards, then, the correction to be applied to the whole set may be deduced.

In addition to the operations of assaying for the amount of silver or gold as already detailed, there are cases where it is required to estimate silver contained in gold, and also gold in silver, such are called 'parting assays.' In the latter, viz., that of estimating gold in silver, it is effected by simply dissolving the metal in dilute nitric acid, and collecting the gold powder left, this is then to be washed with boiling distilled water, and annealed to brightness, when it will be in a state for weighing.

The valuing of silver in gold is somewhat more complex. A double gold assay is made in the usual way, and at the same time another assay pound of the metal is cupelled, but with no silver added. Thus the copper and oxidizable metals are removed, and the button left will be composed of the gold and silver of the specimen only. The difference of weight of this above the parted assay will, of course, be due to silver. But in this operation, not only are comparative assays necessary, but much judgment and experience upon the part of the assayer, or the result will be quite unworthy of confidence. Where these are brought to bear, however, the reports are perfectly trustworthy.

Cases not unfrequently occur where it is of advantage to be able to obtain assays upon very small quantities of metal. These may be well worked in the usual way and with a very delicate balance, but very good approximate assays may be obtained by means of the blowpipe, with the additional advantage of rapidity of execution dependent upon their smallness. Thus a common candle urged by the blast of the ordinary mouth blowpipe will afford the requisite heat in the hands of a practised blowpipe manipulator; but where the gas blowpipe, joined with the double bellows already described, can be obtained, the operation becomes very easy and certain.

A grain of gold will be sufficient for the assay pound; and if to this we add the two to three grains of silver requisite, and 7 grains of lead, the whole mass of metal will at first only weigh 10 grains, or a little more, according to the amount of silver used, a quantity managed with ease.

For this a small cupel of about ¼ inch each way may be employed. This may be rested in a small cavity cut in a piece of sound charcoal. The tip of the flame is first to be directed on this so as to heat it up somewhat; after which, the assay, prepared as in ordinary assays, is to be put in, and when fused by the flame directed upon it, the cupel is to be kept just in that position in the oxidating flame as will carry oxidation on, and at the same time maintain sufficient heat in the cupel for the lead oxide to be absorbed; although much in this operation passes off in vapour. These actions are to be steadily maintained until the assay brightens. It is then removed from the cupel, flatted and rolled. The ribbon may then be annealed by a spirit-lamp, after which it is rolled up, and parted with two acids. These last operations may even be effected in a test tube over a spirit-lamp. The little cornet is, lastly, to be washed into a small porcelain or platinum cup, and annealed over the lamp, when it will be in a state for weighing. And if this operation be well and carefully carried out, very close approximations may be obtained.

As a most delicate balance would be required for these minute weighings, and such an one is not always at hand, I may state that the little instrument described by Mr. Faraday in his *Chemical Manipulation* as Dr. Black's substitute for a delicate balance will answer very well for these weighings, regarding them as approximations, and such an instrument might even be extemporised in situations where a balance could not be obtained.

It consists of a thin slip of pine about 12 inches long and ·3 of an inch broad in the centre, but slightly tapering both in breadth and thickness to each end; in the middle of this a very fine needle is fixed at right angles upon its flat and upper side. Upon each side of this needle or fulcrum, ten divisions are marked at exactly equal distances from each other, starting on each side from the needle. The bearing upon which the beam is to play, is a small piece of sheet brass turned up to equal heights, so that a very narrow plane is thus formed on each side of the beam for the needle fulcrum to rest upon; and as this rises only ¼ of an inch from the little slip of mahogany upon which it is screwed, the play of the beam is very small. The beam, of course, after thus being shaped is to be adjusted so as to equipoise upon this bearing.

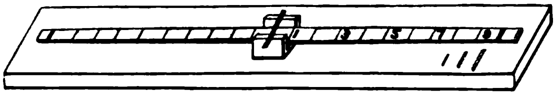
Fig. 62.

The weights requisite for decimal weighing will be three only, viz. 1 grain (as an assay pound), ·1 of a grain, and ·01 of a grain; and these are best formed in platina wire of fit degrees of fineness, as shown in the drawing, where they are represented as lying upon the mahogany base. The ·01 may be of aluminium.

An example may be given to illustrate the method of using this little apparatus.

Placing the grain or assay pound weight upon the tenth or principal division on one end, a slip of the metal to be assayed is cut off, and if of somewhat the shape of the pound, it will be better for accuracy of weighing, as it will lie better upon the beam division, care also having been taken that it should be rather plus, it is to be reduced to the correct weight. Then after cupelling and parting this as above, the cornet obtained is to be placed upon the 10th as before, and now being diminished in weight by the loss of its alloy, the pound must be passed back upon the beam divisions; but supposing the specimen examined to have been of standard quality, even at one back, or division 9, the weight being found too light for the cornet, it is allowed to remain at 9, and the 2nd or ·1 weight is placed on 8, and being found too heavy is passed back, trying a division at a time, until, arriving at division 1, it is found too little. Hence, leaving the 2nd also, upon division 1, the 3rd or ·01 weight is used in the same manner, and passing it back by divisions its real position would be found to be between divisions 6 and 7. Hence, the weight ascertained is thus reckoned. First, the 1000 or pound weight being upon 9 gives the first figure of the report, viz. 9. Secondly, the tenth of the thousand on the first division gives 1 as the second figure. Thirdly, the hundredth of the pound, requiring to be placed at a point between 6 and 7 may be called 6·5. Therefore, the weight will actually be 916·5, indicating the specimen to have been one of standard gold.

It will readily be seen that if necessary this simple instrument might be equally easily applied to trade weighings, by dividing the beam into 8, as the $\frac{1}{8}$th of a carat grain is the smallest denomination, instead of 10 divisions, and then using the 1 grain pound as 24 carats with proportional weights of 22 carats, 2 carats, 1 carat, and 1 carat grain. But the decimal method is very simple, and its weights are easily convertible. The great difficulty in using this little beam with accuracy consists in that of placing the cornet exactly in position on the line. I have managed this by forming a fit-shaped hook in fine wire, and thus hanging it, the point of the hook being on the line, and the cornet hanging just under the beam, and also (of course) using a wire of similar weight on the line on the other arm of the beam as a counterpoise independent of the weights themselves.

But it must be borne in mind that the weighings by such a simple instrument are liable to a considerable amount of error without very great care in its use, and it is therefore only put forward for occasions where a delicate balance cannot be got at. But where it can, very close results are attainable, for the blowpipe operation upon a grain even of metal may be carried out with much of the precision got in ordinary assay quantities, but here the smallness of the weight involves extra delicacy even in the finest balance when used for such work.

CHAPTER IX.

NOBLE METALS.

PLATINUM.

PLATINUM was discovered in 1736 by Anton Ulloa at Choco, in South America, but, owing to the refractory (and in the ordinary way unworkable) nature of this metal, it was cast away,—indeed, got rid of as an incumbrance in regard to mining products, with which it is found; and it is only since the year 1750, when a paper by Woods appeared in the *Philosophical Transactions*, that any account of its nature has been made known; and, although many investigators were, from that time down to Dr. Wollaston's, employed upon it, it is to the latter able philosopher, assisted by the late Mr. Cock, that we owe the peculiar chemical and mechanical operations which have mainly brought it into such an important position in the laboratory both of the experimental chemist and the manufacturer. Berzelius and Vauquelain have also added much to the chemistry of platinum; and as late as the number of the *Annales de Chimie* for August, 1859, publication was made of a valuable improvement in methods of refining, as also of its fusion in considerable quantity. These were effected by Messrs. Deville and Debray in France.

It is found largely in Russia in the Ural district; hence, in that country, it has been employed for coining, also in Peru, Brazil, California, Australia, and in some parts of North America; in all of which it exists as crude platinum ore, and platiniferous sand, the former being in irregular masses, or nuggets, weighing from several pounds, down to small sand-like grains, of a troy grain or so in weight. There are nuggets in Russian collections from a few ounces up to 22½ pounds avoirdupois. In the Berlin cabinet a nugget of 2½ oz. A South American one at Madrid of 2 pounds troy. My friend, Mr. Terry, of Fulham, has one of 2150 grains, or 4½ oz. troy, in his choice mineral collection.

Platinum ore is found in alluvial districts and is a compound of several metals, which, from this association, are known as 'platinum metals.' These are palladium, rhodium, iridium, osmium, and ruthenium. Then, in addition to these, it very commonly contains iron and copper, occasionally manganese, lead, and frequently gold and silver. Again, it has been asserted by Pettenkofer, that there is scarcely any silver free from it, and frequently specimens of gold which come before the assayer for parting, are found to contain platinum; but, in explanation of this, it may be stated that in almost all places where gold is obtained by washing the sand, platinum is found with it, and often in such grains that they can be separated by picking out the latter; and, if they be too much mixed for this, it only remains to amalgamate the mixture, which treatment will dissolve out the gold without touching the platinum.

Any associated magnetic iron ores may also be mechanically separated by the magnet.

The analysis of platinum ore has been perfected by Wollaston, and by Berzelius; and of all chemical operations it is one where the most perfect skill has been exercised. But when it is stated that Wollaston's method embraces some twenty-six, and that of Berzelius twenty-eight, distinct complex operations, it will be seen, when we presently examine them, how much the recent French discoveries already alluded to have simplified the manufacture of this metal, and produce it sufficiently pure for some uses, although not of the purity of the wet method.

The following is a short summary of the chemical and metallurgic operation of Dr. Wollaston, whose work upon the subject, published just before his death, had occupied him some twenty-five years. It may first be premised that the average proportion of platinum in the ore is about 70 per cent, but the quantity ranges from 50 to 80 per cent. The palladium seldom exceeds 1 to 2 per cent.

As the platinum metals are only soluble in nitro-hydrochloric acid, the ore admits of preliminary purification by employing the components of this acid successively. It is, therefore, first heated with nitric acid: thus any copper, lead, iron, and silver, are dissolved. Then, after washing, a second such operation with hydrochloric acid will remove any magnetic iron ore left in it. The ore is now in a fit state to be treated with aqua regia, made from pure nitric and hydrochloric acids; but, in order to prevent the solution of one of the metals, viz. iridium, it is diluted for use with an equal bulk of water. The proportions Wollaston advises are, to 100 parts of ore as much hydrochloric acid as contains 150 parts of actual (dry) acid, mixed with nitric equal to 40 parts of dry. Solution will be complete after three or four days' digestion, but, towards the end, it is always necessary to assist this by a gentle heat. The vessel is then set aside, in order that suspended matter, which is almost entirely iridium, may be deposited. The clear solution is then syphoned off, and to it ammonic chloride, amounting to 41 parts, is added. This throws down a yellow crystalline precipitate, which is ammonio-platinic chloride, which, on heating, will be decomposed, and yield platinum. By this first precipitation about 65 parts of platinum are at once separated from the ore, the weight of the compound salt being, in this case, about 165 parts.

About 11 parts of platinum are left in the mother liquor of the crystals, associated with nearly the whole of the other metals. A clean plate of zinc is then put into it, which will precipitate them all. This deposit is first washed clean, and then redissolved in aqua regia; and to the solution $\frac{1}{32}$nd of its bulk of strong hydrochloric acid is added; after which more ammonic chloride, so as to throw down the remainder of the platinum. This addition of hydrochloric acid last made is for the prevention of the precipitation of any palladium or lead with it. But the palladium may be separated at the first, by first neutralizing the solution with sodic carbonate, and then adding mercuric cyanide: this throws down the palladium, after removing which the addition of ammonic chloride will precipitate the platinum.

As the solution of the ore in aqua regia takes place very slowly, it has been advised, in place of mixing and adding the acids at once, to put the hydrochloric on the ore, and then add the nitric by degrees, as solution progresses; and no doubt acid may be thus economised.

The precipitates of ammonio-platinic chloride are always, however, contaminated with iridium, a portion of which has formed a soluble double salt with ammonic chloride; therefore they are carefully washed with cold water, which will partially remove this, and afterwards pressed slightly between layers of filter-cloth, and then dried.

It now only remains to ignite, in order to separate the ammonia salt; but this requires much care, so as not to use heat enough to agglutinate the reduced metal, the success of the after-working of which mainly depends upon its fine division.

For this reduction it is put into a black-lead crucible and heated, until only the platinum, in fine powder, is left. This is removed, any lumps broken up by the hand, and then rubbed to powder with a wooden mortar and pestle, the rubbing being light, so as not to burnish or condense the powder in the least. It is now sifted through a fine lawn sieve, and mixed with water into a kind of mud. A brass mould is provided, having a cylindrical cavity of 6·75 inches long by 1·12 inch wide at the top and 1·23 at bottom: thus it is slightly taper. A steel stopper or plug enters this, to the depth of a quarter of an inch, being made to fit very loosely indeed, and is put in wrapped in blotting-paper. The mould is well greased and set up in a jug of water, with which also it is filled. Then the platinum-mud is introduced, which, displacing the water, fills every cavity of the mould; the water is then allowed partly to drain out, which it does readily by the blotting-paper round the loose steel plug. After a time the upper surface of the mud is covered, first, with paper, and then a plate of copper, and over these it is slightly squeezed by means of a wooden pestle.

The water being thus pressed out, the mass becomes sufficiently solid to allow of the mould being laid horizontally in a very powerful press: this press (devised by Wollaston) is worked by a lever, by which the steel plug can be forced with an enormous amount of power upon the platinum, and this compression is carried to its utmost limit; after which the plug, and then the cake of platinum, are removed,—an operation rendered easy by the taper form of the greased mould cavity.

The mass is then laid upon a charcoal fire, so as to burn off any grease, and free the porous cylinder from remaining water. Next it is heated in a wind furnace, to a greater heat than the manufactured platinum is expected to bear. It is then removed, and dexterously hammered on the ends, being for this purpose set upright upon the anvil; and Wollaston says, that if it becomes bent, it is by no means to be corrected by blows upon the side, which, if applied, would cause it to crack irremediably, but by careful blows on the extremities, judiciously directed, so as to reduce to a straight line the parts which project.

After forging, it is to be cleaned from any ferruginous scales it may have contracted in the fire, by smearing with a mixture of crystallized borax, and potassic carbonate, which, when in fusion, are a ready solvent for such impurities. It is, lastly, put on a platina tray, and covered with a pot, and then exposed to the heat of a wind furnace, and, on removal from the fire, it is plunged into dilute sulphuric acid for a few hours, to dissolve any adherent flux, when it is ready for manufacture.

The latter, or mechanical, part of the operation is described almost in the words of Dr. Wollaston, and his explanations of the process may be given also. He says, 'Those who would view this subject scientifically should here consider that, as platinum cannot be fused by the utmost heat of our furnaces, and consequently cannot be freed like other metals from its impurities during igneous fusion by fluxes, nor be rendered homogeneous by liquefaction, the mechanical diffusion through water should here be made to answer, as far as may be, the purposes of melting, in allowing earthy matters to come to the surface by their superior lightness, and in making the solvent powers of water effect, as far as possible, the purifying powers of borax and other fluxes in removing soluble oxides.

'By repeated washing, shaking, and decantation, the finer parts of the grey powder of platinum may be obtained, as pure as other metals are rendered by the various processes of ordinary metallurgy, and, if now poured over, and allowed to subside in a clean basin, a uniform mud, or pulp, will be obtained, ready for the further process of casting.'

Notwithstanding the apparent perfection of the process just detailed (and which was the usual manufacturing one up to a very recent date), the manufactured articles from this are very apt occasionally to blister considerably upon the surface, and at times to so great an extent as even after a very few heatings to become seriously injured by it. This is, no doubt, caused by minute enclosures of air, which, by the compression and forging operations are firmly encased in the substance of the ingot; then, when the mass has passed the rollers for manufacture, these air-bubbles are brought sufficiently near the surface to raise blisters in the metal, when somewhat softened by heat. A large manufacturer of platinum told the author that it was his custom to replace vessels supplied if this state of things occurred when they were newly made, although, of course, at much loss to himself.

Then again, the platinum so prepared is apt to retain a notable quantity of iridium in its composition, owing to the difficulty of washing it out of the precipitated double salts: thus remaining portions are reduced by heat with the platinum. In the uses of the metal in the experimental laboratory for vessels, this alloy is rather beneficial, for if a due proportion of iridium be employed to alloy platinum, the metal is not only more resistent of high temperatures, but also less easily acted upon by chemicals. Thus, excellent small vessels may be formed of the crude platinum by fusion, by the method presently to be described, in which way osmium and palladium are driven off, being volatile, and a natural alloy of platinum, iridium, and rhodium left.

Where platinum is needed perfectly pure from iridium, it may be obtained by precipitation of the metals by means of potassic chloride, the precipitate after washing is fused with twice its weight of potassic carbonate. Thus the iridium is oxidized, while the platinum is reduced to the metallic condition. By boiling the whole in water, all potass salts are removed, and then, on treating the residue with nitro-hydrochloric acid, the platinum is dissolved, leaving the insoluble iridium oxide untouched by it. If any iridium is yet found in the product, this operation may be repeated. Potassic cyanide solution may also be used for the separation, for, on digesting the precipitate in it, the iridium salt will dissolve while the platinum one is insoluble,

A process very analogous to Dr. Wollaston's is employed in Russia, in order to render platinum malleable for coinage purposes. It is triturated in a brass mortar, sifted, and then pressed together under a steel die by means of a powerful screw press.

Deville and Debray, after working upon the subject for nearly five years, have substituted for the wet processes in use a dry metallurgic operation, whereby the refining is effected in an analogous manner to the operation already described for silver refining, having first taken advantage of the fusibility of certain alloys of platinum to carry it out.

They take the ore, and in quantity up to 2 cwts., and with it about its own weight of galena (plumbic sulphide). These are then heated in a reverberatory of just sufficient dimensions, the sole being basin-shaped, and constructed of very refractory clay, upon a basis of fire-bricks. The ore being heated to bright redness, the galena is thrown in by portions at a time, and constant stirring is kept up so as to thoroughly mix the ore and galena. This done, 2 cwts. of litharge is next added, in similar manner. This supplies oxygen to the sulphur of the galena, and they pass off as sulphurous anhydride, while the whole of the lead, thus being reduced, combines with the platinum metals, but at the same time introduces into the mixture any small portions of silver originally contained in the galena. A little glass is used as a flux during this part of the operation. After standing in the state of fusion for a time an upper bath will be formed, containing an alloy of lead with platinum, palladium, and silver; the other metals, being unacted upon by the treatment, will by their superior density subside to the bottom, after which the platinum alloy is carefully ladled off for future refining operations.

The first of these consists in cupelling the platina lead upon a test whereby the greater part of the lead is disposed of by oxidation. But the difficulty of separating the lead by the cupellation depends upon the melting point of the alloy rising as the lead separates, so that towards the close of the operation a very high temperature is essential to maintain the bath in the liquid condition. The metal therefore needs very careful after refining.

The effecting of this depends upon means whereby they have been able readily to melt platinum, and thus bring the operation into the class of an ordinary metallurgic one. The essential part of the apparatus consists of a kind of furnace, shaped out of well-burned lime, and which may be somewhat compared to a cupel in its use in this process, for it not only absorbs impurities, but assists in getting rid of them. Then, as an exceedingly high temperature is employed, the bad conducting, and good radiating power of lime are most useful. For, notwithstanding the metal being, in the interior, at a full white heat, the exterior will not be, by any means, extraordinarily hot; while, by radiation, the interior crown of the furnace will much assist the fusion.

Deville's smaller furnace (fig. 63) consists of two pieces of lime joined for use in such way as to form a kind of basin with a hollow cover. The lower piece is hollowed out into the basin, for the reception of the metal: it is solid (or may be formed of blocks closely fitted), in either case being like the top piece, also firmly bound round with stout iron wire or bands. The upper cylindrical cover piece has a corresponding cavity hollowed out, and in the centre a round taper hole, tapered slightly from above downwards, for the introduction of a blowpipe jet; a joint opening is also formed at one side for the introduction of the portions of platinum; and the lower half forms a spout for pouring the fused metal.

The heating apparatus is an oxyhydrogen blowpipe of large dimensions, and of the form already described as an air blowpipe

(p. 90). The outer and lower tube carries hydrogen (or coal gas), and the inner and upper one, in place of air, throws a jet of oxygen into the middle of the flame, both supplies being capable of close regulation by means of stopcocks. The tubes themselves are formed of copper, each tipped with platinum.

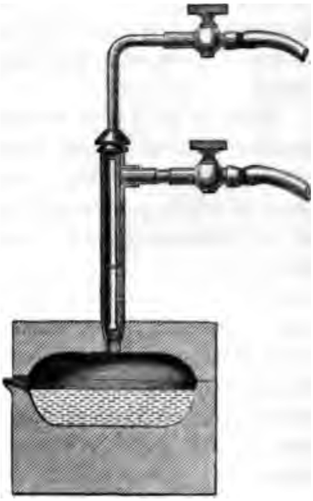
Fig. 63.

Suppose the object be simply to fuse some scrap platinum, and cast it into an ingot. The lime furnace is first put together, and then the hydrogen jet lighted, and turned into the upper opening formed for the blowpipe; oxygen is then supplied, and the whole apparatus heated as strongly as can be effected. The platinum is then introduced in pieces by the hole at the side; the furnace is at this time cooled down slightly, but the authors say that the metal runs down immediately it enters the furnace. The heat is maintained for a time, after which the metal is ready for casting.

But the great use of such a furnace is for the refining of the platinum obtained by cupelling platinum lead, and for this end it is heated upon the bed of lime, until no more vitreous matters are seen to rise to the surface, the gases are then gradually turned off, beginning with the hydrogen, and in such a manner as always to leave the oxygen somewhat in excess; thus the mass solidifies, and at length the flame may be quite extinguished; but the metal is generally poured from the lime cupel and cast in an ingot mould, formed of coke or of plates of lime; and the authors say that thick cast-iron moulds may be used, if they are well coated over with plumbago; the platinum being kept fluid by the jet until poured, for which latter purpose the jet and upper section of the mould are removed, and the lower one tilted by tongs, or by a proper arrangement for the purpose, so as to pour its contents steadily into the mould. The great difficulty in pouring, however, consists in being able at the same moment to discern between the mouth of the mould, and the dazzling white surface of the molten metal.

From 7 to 8 lbs. avoirdupois may be operated on in this manner without danger from the apparatus giving way, and the authors describe a larger and modified apparatus for large quantities, in which quantities of 20 to 30 pounds are refined; a couple of oxyhydrogen flames being employed. The time occupied is from 40 minutes to an hour. At the intense heat used, any palladium or osmium is volatilized, as also small quantities of lead, and of gold or silver, when present. But the metal left is not pure platinum, for it retains those metals of the ore, which escaped separation by subsidence in the reverberatory operation, or were not volatilized during refining. And although Deville's process has great advantages, yet the wet one first described affords the purest metal.

This has been demonstrated in the construction of Siemens' pyrometer coils, for that gentleman found that the wire made from platinum obtained by Deville's method was useless from its impurity, and he was therefore obliged to employ such as is made from platinum got by Wollaston and Cock's method.

Deville and Debray have perfected a melting furnace upon the same plan. It is formed of three blocks of good sound lime (fig. 64). The lower one forming the base (*a*) is a circular plate of about 2⅛ inches thick. This carries a cylinder (*b*) about 4½ inches in height, and having four apertures (*c*) at the lower part for the escape of the gases, vapour, &c., evolved during combustion. This piece is the furnace chamber. Upon its upper end is placed a third piece (*d*), which covers the chamber, and is about 3 inches thick, and perforated by a cylindrical hole in the centre for the passage of the compound jet of the blowpipe (*g*), as in fig. 63. Inside the chamber is placed an outer crucible, formed also of lime, and provided with a conical lime cover (*e*). This stands upon a small lime support (*f*), and encloses the actual crucible, which is formed of gas coke, and has a cover of the same material. Each portion of the furnace is firmly tied together with a binding of iron wire to prevent separation or cracking; and, in using, the heat has to be very gradually got up, but the action of the furnace is very rapid when fairly heated. Much has been done by such means in melting bodies formerly considered almost infusible. Messrs Johnson and Matthey exhibited some results at the International Exhibition of 1862, where they had a fused ingot of platinum weighing 2½ cwt.; a cake of iridium of 27½ oz.; and a button of rhodium weighing 1 oz.

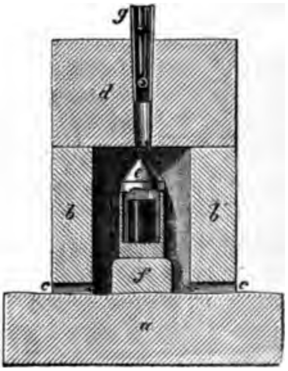

Fig. 64.

The black powder known as platinum black is really pure platinum in exceedingly fine division, and may be obtained by several methods. A dilute solution of platinic chloride may be acidulated with hydrochloric acid, and a plate of zinc introduced, when the platinum will fall in this form, but is apt to be rather more spongy than that reduced by organic bodies. The black should be boiled in nitric acid, and then washed with water.

It may also be separated from platinic chloride by heating with sugar and sodic carbonate. Four parts of chloride are treated with 1 of sugar and 12 of sodic carbonate in crystals. The sugar is transformed into water and carbonic acid, and sodic chloride is formed. The mixture is heated in a water bath to boiling nearly; and the flask must be often shaken during the decomposition. The presence of nitric acid hinders this reaction.

A common method consists in employing platinous chloride, dissolving it in a concentrated solution of caustic potass, boiling in a large vessel, and adding alcohol by degrees. Carbonic acid escapes with effervescence, and the metal falls. It is removed, washed with alcohol, solution of potassa, and hydrochloric acid successively; then with water, and carefully dried.

Small platinum vessels are readily made by pressing the pulverulent platinum of Wollaston's process, either dry or moist, into a fit mould, the stamp for the interior being driven either by a press or a hammer. They are next heated in an air, and afterwards more strongly in a blast furnace, and, lastly, finished by beating red-hot upon an anvil.

The properties of platinum are as follows:—It is of a white colour, but not so pure a white as silver. In hardness it is about the same as copper. It is exceedingly ductile, and may be drawn into very fine wire; and Wollaston, by forming a coating of silver upon a fine platinum wire, and then drawing this through the draw-plate, obtained a fine compound wire, from the outside of which he dissolved the silver, and so left a platinum wire finer than any wire hitherto made. His object was to endeavour to substitute wire for the spider's web usually employed in micrometers. His method has been already described at page 12. Platinum exceeds all metals, excepting iron and copper, in tenacity. Its specific gravity ranges from 20·8 to 21·7. It welds very readily at a full red heat, so that injured platinum vessels may readily be repaired by heating, and then welding on a piece of foil also heated, the operation being performed upon an anvil, as in ordinary welds of iron. Indeed, Wollaston's process for manufacturing platinum is based entirely upon this welding capability. But to succeed perfectly with manufactured platinum, the surface should be clean, but roughed, for bright surfaces do not weld soundly.

It is nearly the most infusible metal, those which excel it in this respect being some associate metal, as rhodium, for example. It requires the oxyhydrogen blowpipe for its fusion, and at a very high temperature absorbs oxygen, and spits or springs like silver on giving it up on cooling. It is quite unoxidized in the air and untouched by simple acids, the proper solvent being chlorine (as evolved by aqua regia), although the gas itself is inactive upon it.

When platinum is alloyed with silver, however, it will be largely dissolved in nitric acid; hence, where gold contains a small proportion of platinum, the latter may be separated by quartation of the gold with silver, and a subsequent free boiling in nitric acid. The acid, by this, will acquire a deep straw-yellow colour. The resistent qualities of this metal give it its great value for chemical vessels, but these require care in using. Thus we cannot heat a metal in them to near its fusing point, or they are very liable to alloy with the contained metal. Then, some oxides are very destructive to them, especially if associated with any body (as carbon) which is capable of taking their oxygen, so as to reduce the metal which then alloys with the platinum. The alkalis and alkaline earth destroy it at a red heat, as also does nitre. Symbol, Pt. Atomic weight, 197·1.

Platinum forms two oxides. 1st. Platinous oxide is a protoxide. Formed on adding solution of potassa to platinous chloride; after digestion, a green liquid results, from which a black hydrated oxide falls on neutralizing with sulphuric acid, for it is soluble in excess of alkali. It forms unstable salts with acids. Composition, Pt. O. Atomic weight, 213. 2nd. Platinic oxide (the binoxide) is precipitated by sodic carbonate from platinic chloride, but as the oxide will combine with alkaline bases, the soda salt is only added up to half the amount otherwise necessary. Thus a brown hydrate falls capable of forming double salts with alkalis, and with acids forms tolerably permanent salts. Composition, Pt. O_2. Atomic weight, 229.

There is a protochloride, or platinous chloride, Pt. Cl_2, which is obtained in a precisely analogous way to the corresponding chloride of gold; but the bichloride, or platinic chloride, as formed in the ordinary solution of platinum, is the important one. It is obtained by heating the metal in aqua regia, and subsequently evaporating the solution carefully at a low temperature. Thus a deliquescent cake of a reddish-yellow colour is usually obtained, deeper in colour as the water is expelled. It is from this that all the platinum compounds are obtained, either directly or indirectly. It is soluble also in alcohol; and this solution forms our best test for the presence of potash or ammonia. And (as has already been shown) if the ammoniacal precipitate be heated, spongy platinum alone remains. The composition of platinic chloride is $Pt. Cl_4$, and its atomic weight 339·1.

There are two sulphides of platinum; the first, or platinous sulphide, may be formed by acting upon moist platinous chloride by dihydric sulphide. The second cannot be prepared by the usual method in such cases, viz. by passing the gas into platinic chloride, for we do not thus get a true bisulphide thrown down, but a compound of platinic chloride and sulphide. When, however, the acid gas is added to the sodio-platinic chloride, a bisulphide is precipitated. This must be filtered out and washed with hot water, and then dried in vacuo. When first thrown down, it is a brown powder, which becomes black upon drying. At a dull red heat the sulphur is driven off and platinum left.

Alloys.—Worked platinum cannot be amalgamated with mercury, and the only method of forming platinum amalgam consists in rubbing finely-divided platinum (such as that reduced from the ammonio-chloride) and mercury together in a warm mortar: the combination of the two will be accelerated by moistening the two metals with water, acidulated with acetic acid. It forms an unctuous amalgam, increasing in solidity in proportion to the amount of platinum it contains. The more unctuous amalgam may be employed, just as the gold amalgam is, in water-gilding; and metals may be platinized in an analogous way to that by which they may be water-gilt, for the mercury is driven off at a strong heat, and platinum is left.

Platinum alloys with silver in all proportions; the latter metal loses somewhat of its whiteness, becoming harder by the association. Hot sulphuric acid will dissolve the silver from such an alloy, but if nitric acid be used for this purpose, it will dissolve more or less of the platinum also.

With gold, an excess of platinum renders the alloy infusible in a wind furnace —2·5 of platinum to 1·0 of gold, for example.

Equal weights will give a very malleable alloy, having very much of the colour of gold. One part of platinum to 9·5 of gold does not much diminish the yellow colour of gold, while it affords an alloy of the same density as platinum.

A soluble salt of platinum may be discriminated by the following reagents:—

1st. Dihydric sulphide will throw down, after a time, or at once on heating, a blackish brown precipitate, insoluble in nitric or hydrochloric acid alone, but soluble in them when mixed.

2nd. Ammonio-hydric sulphide produces the same precipitate; but this will be slowly and not easily dissolved by excess, and reprecipitated upon the addition of acids.

3rd. Potash, or ammonia, each throws down a very characteristic yellow crystalline precipitate, soluble when aided by heat, but readily precipitated in a cold solution, especially if it contain any hydrochloric acid. The potassa precipitate is soluble in a large excess of the precipitant, and the ammonia one, when dried and heated, gives metallic platinum.

4th. Soda precipitates brown hydrated platinic oxide from platinic salts: this is soluble however, if any excess of soda be added.

5th. Stannous chloride, added to solutions of platinum salts, gives an intense brown-red colour to them, but does not throw down any precipitate, they must however contain hydrochloric acid in excess for this reaction.

6th. Ferrous sulphate does not precipitate platinum.

For the quantitative estimation of platinum, we may separate it from almost all metals by the addition of ammonic chloride.

To a platinum solution the chloride is added, and subsequently a little alcohol; if this precipitate be collected, and then washed with dilute alcohol, in which it is insoluble and then dried, it will be ready for weighing, and every 100 parts will contain 44·28 of platinum.

Supposing platinum to be contained in an alloy of gold and silver, it may then be estimated after the latter are separated in the way already described; and as the oxalic acid by which the gold is thrown down does not precipitate platinum, it will be left in the solution for subsequent precipitation. For this Miller advises neutralizing the solution by sodic carbonate, and then precipitating the platinum in the metallic state, by boiling the liquid with a soluble formiate.

When assays are made of gold containing platinum, much care is requisite, or the report will be given too high, from its retention. If the quantity associated with the gold does not amount to more than $\frac{1}{25}$th, it will be separated during the acid parting work (Vauquelain says 30 to 40 of platinum to 970 or 960 of gold will have the platinum quite separated in the acid work); but if above these quantities, extra care must be taken in each stage; and when the platinum reaches 12 per cent, or more, it is scarcely possible to separate it in the ordinary way.

Its presence is indicated by the dull working of the button in the cupel, by want of brilliancy in the play of colours and final clearing of the button; and this will be left dull and crystalline upon its upper surface. Then, on parting, the acid will become more or less of a straw colour.

It is well, upon these signs, to commence a fresh assay, giving it rather an extra quantity of silver, a stronger furnace heat, and after laminating very thinly, employing a brisk boiling in the acid apparatus. Thus any quantity short of 12 per cent will be dissolved out.

CHAPTER X.

NOBLE METALS.

PALLADIUM.

PALLADIUM is at times found native in company with platinum, but the grains may be distinguished from the latter by the fibrous structure which they exhibit. They are in a comparatively pure state. It may be obtained from platinum ore, after the separation of that metal, as it contains about 1 per cent of palladium, and it is also associated with some of the gold obtained from Brazil as an alloy of gold and palladium; and this and similar ores have been great sources of it, ranging in amount in them from 5, up to 10 per cent in some few; hence, a few years since, this metal was to be purchased at about 18*s.* per oz. But, at the present time, this means of supply having failed, its price has risen to about 8*l.* per oz.

It is separated, in platinum working, after the platinum has been thrown down from the ore solution (p. 293), by treating the residuary acid liquor with mercuric cyanide. A white flocculent precipitate is thus thrown down, which is palladious cyanide. Heating this with sulphur separates the cyanogen, and palladious sulphide remains, which may be decomposed and its sulphur driven off by heat; or the cyanide is decomposed by heat alone, the cyanogen being driven off.

The process usually adopted for the separation of palladium from Brazilian gold was devised by Cock. The gold dust is fused with an equal quantity of silver, and some nitre. The latter oxidizes certain base metals, and, combining with earthy matters, forms altogether a slag, from which the alloy is poured away. This is again fused with a second portion of silver, so as to quartate the gold, and the mixture is poured from the black-lead crucible into water for granulation. The alloy is then parted with twice its weight of nitric acid, of 1·30 specific gravity; and, when action has ceased, this is replaced by a second quantity, and the parting operation carried on for two hours longer. The gold removed, the acid liquors contain the palladium and silver, with any copper present. To this liquid common salt is then added, to throw down the silver as chloride. And when this is removed, by decanting the supernatant liquid from the subsided precipitate, a quantity of zinc is placed in the liquid: by this the palladium and copper are thrown down as a black powder. This is next removed, and dissolved in nitric acid; after which the solution is supersaturated by ammonia. Thus palladium and copper are held in solution, their oxides being soluble in ammonia, while small portions of platinum, lead, and iron, will be thrown down. Lastly, the filtrate is treated with hydrochloric acid, which separates the palladium as a double chloride with ammonia; this, washed and ignited, will afford pure spongy palladium, as a grey mass. This, however, is not malleable, and for the acquisition of this quality it needs further treatment. It is, therefore, generally fused with sulphur, and the sulphide so formed treated at a second fusion with a little nitre and borax, the crucible having free access of atmospheric air allowed to it. This cleanses it, and it is then taken out and roasted on a porous tile, and the pasty mass resulting pressed into a cake, roasting being kept up so as to expel the sulphur as sulphurous anhydride, and leave the palladium again as a spongy mass. When nearly cool, it is gently condensed under the hammer, then heated again, and again hammered, so as to solidify the mass gradually, without which care it would still exhibit brittleness. Gmelin says, that, in this last state, the brittleness results from retention of some of the sulphur.

Properties.—A white metal, much resembling platinum, but having a specific gravity of 11·8. It is less ductile than platinum, and apt to crack at the edges when rolled. Although the most fusible of the platinum metals, it is not easy of fusion, for it requires nearly the heat needed for fusing malleable iron; when liquid it evaporates in a green vapour, which, on condensing, forms a dark-brown dust, composed of a mixture of metallic palladium and its oxide. If heated and fused in an oxidizing atmosphere, it vegetates on cooling, just as silver does. It does not oxidize in the air, unless the temperature be considerably raised, and then the surface may be again restored by a stronger heat, which drives off the newly-formed oxide. Of the three mineral acids only nitric dissolves it readily, but in this or in aqua regia it dissolves on heating, affording a deep brown-red solution. Iodine acts upon it, so that platinum may be distinguished from palladium by heating a drop of iodine tincture upon it. The former is untouched, but the latter shows a stain. Symbol, Pd''; atomic weight, 106·5.

Palladium unites with oxygen in three proportions, forming a suboxide, $Pd_2 O$; a protoxide, or palladious oxide, $Pd O$, which is the base of the salts of palladium; and a dioxide, or palladic oxides, $Pd O_2$.

Palladium also combines with chlorine, and two chlorides exist,—a protochloride, or palladious chloride, $Pd Cl_2$, and a perchloride; the first may be crystallized, but the second, palladic chloride, or $Pd Cl_4$, exists only in solution.

A sulphide of palladium is formed when dihydric sulphide is added to a palladium salt: it falls as a black precipitate composition, $Pd S$.

Alloys.—With mercury palladium forms a grey plastic amalgam, and when union takes place it is attended with evolution of heat, hardening quickly as it cools. It may be readily made by adding pure mercury to spongy or pulverulent palladium in a mortar, and when union is taking place removing it and placing it in linen, quickly squeezing out any excess of mercury, as the amalgam so soon sets tolerably hard. Wollaston advised the formation of it by decomposing a palladium salt by excess of mercury, when, by agitating the two together for a considerable time, a soft amalgam is obtained. If the palladium salt is in excess it will form a grey powder, consisting of two proportionals of palladium with one of mercury, and so permanent as to require a white heat for getting rid of the whole of the mercury.

Silver and palladium may be combined in any proportion, and when in the proportion of one part of palladium to two of silver, the metal retains the exceedingly brilliant polish which may be given to it. This alloy was much employed when the cost of palladium was less, being an excellent one for polished surfaces of instruments requiring to be graduated.

Gold and palladium form a hard grey alloy when combined in equal proportions. One part to four of gold forms a white alloy. One part to six of gold is but slightly coloured by the latter. They are all very brittle.

Platinum and palladium in equal parts form a grey alloy, about as hard as bar-iron, and which fuses below the fusing point of palladium.

Salts of palladium may be discriminated by the following tests:—

1st. Dihydric sulphide, or ammonio-hydric sulphide, gives a black precipitate of palladious sulphide, insoluble in alkaline sulphides, but soluble in hydrochloric acid.

2nd. Potash, or soda, throws down a red subsalt from solutions of palladium salts, and on the application of heat; this subsalt will be dissolved in any excess of alkali present.

3rd. Ammonia and its carbonate throw down a copious flesh-coloured precipitate, an ammonio-chloride soluble in excess, but from palladious nitrate ammonia gives no precipitate.

4th. Ferrous sulphate reduces palladium salts after a time, and, as with gold, heating the solution facilitates the reduction, but if the solution is very acid, action is proportionally slow; the precipitated metal covers the sides of the vessel in a film.

5th. Stannous chloride gives a brown precipitate, which is soluble in hydrochloric acid, giving a bluish green solution. On largely diluting this, it becomes reddish brown.

Lastly, mercuric cyanide is the characteristic test. This precipitates a yellowish-white cyanide, which becomes white on standing, and is soluble in hydrochloric acid.

The estimation of palladium quantitatively is generally made from this precipitate, for, by mercuric cyanide, we have the means of separating it from all the noble metals, and, indeed, from all others, if we except lead and copper. If, then, a solution of the alloy be made in aqua regia, silver will be separated during the solution. The acid of the filtered solution is next saturated with sodic carbonate, and mercuric cyanide added; lastly, the separated cyanide is heated, and the palladium obtained by its decomposition is weighed directly as metal.

CHAPTER XI.

LEAD.

LEAD has been known from very remote times, but there seems to be reason for believing that the name, as found in early writings—the Bible, for instance—did not signify the metal now bearing this name.

The chief ore is a sulphide called galena, the average composition of which may be assumed as of about 80 parts of lead associated with 13 of sulphur. It is in fact a protosulphide, and consequently, if pure, should have the composition of 81·61 per cent of lead with 13·39 of sulphur. But sulphides of antimony, copper, zinc, arsenic, and iron, are also found in small proportion in it. And it is further associated with quartz, fluor spar, calc spar, and heavy spar or baric sulphate.

Galena invariably contains silver, in the form of argentic sulphide, and the proportion of silver is subject to great variation. One-third per cent constitutes a very rich ore. Such a one was shown in the Exhibition of 1862. It was a Swedish ore, containing rather above 100 ozs. of silver per ton, which would equal one part in 326. The average, however, of ordinary galenas is about 0·002 per cent.

Percy,* on the authority of Mr. Radcliffe, mentions the extraordinary richness of Peruvian galenas in silver, stating that it varies in the rich kinds from 170 to 1138 ozs. per ton, and that the latter contained further half an ounce of gold per ton; and Percy states that he has never found a lead ore containing silver which did not also contain gold, and 'probably in the state of sulphide.' Galena is known by the names of blue lead, specular galena, argentiferous galena, &c., dependent on appearance, association, &c. The latter, containing silver, is not easily distinguished by any great external difference. The purer the galena the smaller is the amount of contained silver.

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* Percy's *Metallurgy*, vol. iii. page 273.

Galena is a crystalline ore, its primary form being the cube; but, as would be expected, it is frequently found in octohedra. It crystallizes at times in very beautiful groups of cubic crystals, having much metallic lustre.

It is the principal source of English lead, and is found in Derbyshire and Cumberland, in the carbonate of lime formations; in Wales at Holywell, in Flintshire; in Cornwall it is found traversing clay slate rocks; in Scotland it is also obtained largely at Leadhills in Lanarkshire; also in the Isle of Man, and in Ireland; largely in Spain, in the German States, and Sardinia; and in smaller quantities in France and Belgium.

Lastly, in the United States, and latterly considerable quantities of plumbic sulphate, containing much silver, have been brought from Australia.

The rarer minerals of lead are almost invariably found in association with galena. They are, native oxide or massicot, chloride, sulphate, carbonate, phosphate, and chromate of lead.

Before smelting the ore, it is assayed in order to ascertain the amount of lead present, and of the several methods of assaying galenas, that wherein the ore is simply fused in contact with iron, is by far the best. Heating with iron sets free the lead at once, the sulphur of the ore uniting with the iron to form a sulphide. In some cases an earthen crucible is used and metallic iron added, but the most usual plan is that of heating the ore with a flux in a wrought-iron crucible, in which case the requisite metal for decomposition is furnished by the vessel itself. The fluxes used are some alkaline one for the dissolving and separation of earthy matters, and a little borax, the latter to assist in cleansing the metal set free, and thus promoting the formation of a compact button.

Supposing an earthen crucible is employed. The ore is first powdered and dried. The weight for assay is then taken, and 250 grains is a fair quantity to operate upon, but if the ore is not rich, as much as 500 grains must be employed. If 250 grains are considered sufficient, it must be mixed with 350 grains of black flux, or some analogous flux, as for instance a mixture in the proportion of 1 part of powdered argol with 7 of sodic carbonate, and of this mixture about 150 grains would be used. A clay crucible having been heated to dull redness, the mixture is introduced; about 50 grains more flux is next put in, then a few pieces of good iron (and horse shoe-nails are often employed as being made only of the best quality of iron). Lastly, about 60 or 70 grains of fused borax is put upon the top of all. Of course if 500 grains of ore is operated upon, the amount of fluxes, &c. are increased in like proportion. The crucible is then placed in a wind furnace, and heated gradually to full redness for about ten minutes, after which the remaining iron is removed, the whole allowed to cool, when the pot is broken and the mass struck a sharp blow on the side with a hammer; this compresses the button and breaking the slag detaches it. The slag being hard and brittle, but the button soft. It is better to operate thus than to pour the crucible contents into a hemispherical mould, and then separate the slag, for it is difficult to pour without risking some beads of metal remaining adherent to the pot.

When the assay is made (as it commonly is) in a wrought-iron crucible, the operation is carried out in the same way, omitting, however, the introduction of iron. There is some trouble in obtaining these crucibles of good make and quality. Percy says of the assay in iron crucibles, 'From long experience of this method of assaying, in the Metallurgical Laboratory of the School of Mines, and from an experimental comparison of it with other methods, we have come to the conclusion that it is the best.'* An iron dish is often similarly used.

A dry assay of lead ores without iron may be made as follows. An accurately weighed portion (dried and powdered) is mixed with three or four times its weight of dry potassic carbonate. This is put into a small clay crucible, and covered with a layer of dry sodic chloride. It is next introduced into a muffle, and heated to a high temperature for half an hour. A button of lead will subside, which, on removal and separation of the slag, may be weighed. But this method requires much more care and time than the iron method, and is not often used, as it only succeeds in experienced hands.

Several wet methods, by means of standard solutions, have been devised; but they are mostly tedious, and open to small sources of error, and hence cannot compare with dry ones either for speed or accuracy.

Of these, Dumonte's may be offered as a more simple example. He dissolves the sample in nitric acid, evaporates it to dryness, re-dissolves in potassa solution; then, after filtering, estimates the lead by the amount of a standard solution of sodic sulphide required to throw it down as plumbic sulphide, delivering it from a burette, and heating between each addition in order to clear, until the lead solution is quite saturated. The standard solution is made by dissolving about 500 grains of sodic sulphide in a quart of water, and ascertaining its value by testing it with a weighed quantity of pure lead.

If a wet method is needed, the ordinary analytical one of converting the lead into sulphate may be used. A quantity of ore is powdered, and a sample of about 25 grains carefully weighed from it. This is treated with strong nitric acid. When decomposition ceases, a few drops of strong sulphuric acid are added, and it is to be evaporated until all the nitric is driven off. The metals will thus be converted into sulphates.

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* For detailed account of the method see Percy's *Metallurgy of Lead*, page 107.

The mass is next digested in water to dissolve out soluble sulphates, and the insoluble residue filtered out, and washed with water containing a little sulphuric acid. The insoluble matter is next dried, ignited in a small porcelain crucible, and weighed. It is next removed and digested in a solution of tartrate of ammonia, or of acetate of ammonia, added in successive portions; this will dissolve out the plumbic sulphate, leaving any baric sulphate with other insoluble bodies, as the oxides of tin and antimony, quartz, &c.

The part undissolved of the whole is again filtered out, well washed with boiling water, and again dried, ignited, and weighed. The difference between the two weighings is the amount of plumbic sulphate which was present in the first weighed matter, and from this the weight of lead may be calculated.

The smelting of lead in the reverberatory furnace has been long in use. By it almost all ores, except very refractory ones, are worked. It is most effective for ores which contain but a small amount of silica, with not a large admixture also of foreign sulphides. The ore is first sorted and freed as much as possible from such siliceous matters, and then ground and washed for the same object, when it is ready for the smelter.

The principle of this operation consists in heating the ore in such a manner, with free access of air, as shall convert portions of the plumbic sulphide into plumbic oxide, and also plumbic sulphate, by oxidation of both lead and sulphur of the galena. The portions so changed react upon some crude or unchanged ore, and the sulphur and oxygen of the combinations so engaged being just in the proportions to produce sulphurous anhydride, this gas is formed and evolved, and the metallic lead set free.

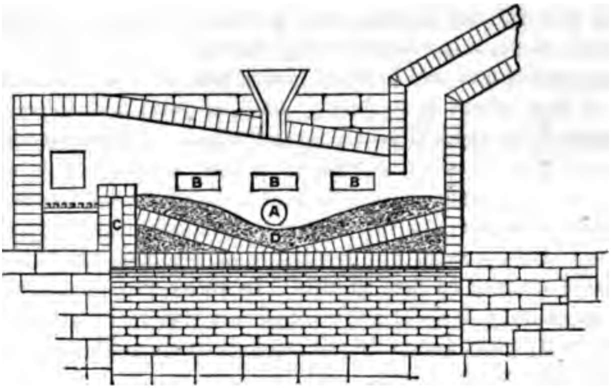
The changes may be thus symbolised. First in the production of plumbic oxide $2\ Pb\ S + O\ 6 = 2\ Pb\ O + 2\ SO_2$. And for plumbic sulphate, $Pb\ S + O_4 = Pb\ SO_4$.

Then in the reaction of plumbic oxide and sulphate upon crude sulphide, $2\ Pb\ O + Pb\ S = SO_2 + 3\ Pb$; and $Pb\ SO_4 + Pb\ S = 2\ SO_2 + 2\ Pb$.

In the whole of these reactions five atoms of plumbic sulphide, with ten atoms of oxygen, set free five atoms of metallic lead, forming five of sulphurous anhydride at the same time.

The reverberatory furnace employed has a bed of about 10 feet by 8, formed generally of old slags of former operations. It is well depressed at one side in the centre at D, and at the lowest part a tap-hole, A, is formed for the running off of the metal, for receiving which there is an iron basin outside the furnace at the tap-hole. A series of openings, B, are also formed in each side for air admission, as also for working the charge. There is a bridge,

Fig. 65.



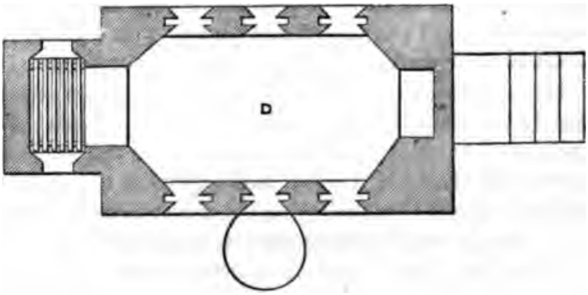


Fig. 66.

C, of at least a foot between the furnace and bed; and at the back the flue-opening, G, is placed as low as 9 inches above the bed. This is provided with a damper to check draught, and as the lead fumes are very liable to partially choke the horizontal part, its top is always provided with movable tiles for the clearing this out, and thus much metal is recovered. The flue terminates in a shaft of about 60 feet high.

In this furnace a little over a ton of ore is worked upon; generally alone, if it contain earthy matters, in such relative proportion as will flux well together; but if not, then the ore is mixed with a flux, which is usually about $\frac{1}{30}$ of lime; and these, after charging in, are spread evenly upon the bed. The furnace having worked off a previous charge (and the working of a charge occupies about five hours in all), it will be somewhat cooled down by its removal, &c., but the heat is but slightly raised, by partial closing of the openings, in order that a slow calcination of the new charge of ore may be first effected. In about two hours any rich slags or skimmings of former workings are thrown in, and as these will speedily yield their lead the tap-hole is opened for running it off into the receiving pot.

The smelter next turns over and rabbles the charge, so as constantly to bring fresh portions in contact with air for the necessary conversion of such portions into oxide and sulphate.

This stage over, he raises the damper and closes up the furnace sufficiently to raise the temperature to bright redness. Reaction then sets up between the plumbic sulphide and the oxide and sulphate, and the charge effervesces, and quantities of sulphurous anhydride are evolved, thus producing the effervescence. The lead now begins to flow down into the depression of the bed, and to keep up the reaction the slag is kept from fusing down also, but rather pasty enough to allow of the changes going on. The heat is therefore somewhat lowered, and as the charge melts and sinks down, a little quicklime is at times put in and the heat then again raised. Some portions of this set free oxide of lead by decomposing any silicate present, the lime itself becoming calcic silicate. But its chief use seems to be the prevention of too ready fusion of the charge, and for its retention in that pasty state which will admit of the constituents reacting perfectly upon each other.

As a last step, the heat is raised to the highest point needed, and in about three-quarters of an hour the metal subsiding in the bed is run out into the receiving pot, after which the slags remaining are treated with enough lime to 'dry' them, that is, to render them sufficiently solid to rake out at the slag opening.

The pot of lead is usually covered with some small coal, which, after stirring with it, is skimmed off, and, as above stated, put into the next charge just after calcining, together with the plumbic sulphide produced and separated from the reduced lead.

The slag run from the furnace amounts to about 25 per cent of the charge, and when (as it generally does) it contains unseparated lead, it is subjected to an after operation for its removal, in a slag hearth, or at some works in a cupola furnace. The consumption of coal amounts to about 12 cwt. per ton of ore.

At places in Cornwall, as also at some Continental works, the calcination and reduction of the ore are carried on by two separate operations, and in distinct reverberatory furnaces. The first or calcining one is large, and in it the ore is roasted with occasional stirring; this often lasting about 18 hours or so. This roasted ore is next melted in a smaller furnace, wherein, after fusion, it is covered with a quantity of quicklime and some anthracite, and heated with about 5 per cent of iron in pieces. This latter acts upon the plumbic sulphide, and sets the lead free, and has the effect, moreover, of so completely decomposing the ore that the slag subsequently run off will be nearly free from lead. The lead is first tapped off, and after this a regulus, from which more lead is obtained by subsequent smelting; then, lastly, a separated and worthless slag is removed.

In the north, in Cumberland, Durham, Northumberland, and also in Scotland, lead is smelted on the Scotch or ore hearth, which is a small blast furnace, or rather forge, supplied with the tuyere of a blowing apparatus, the whole covered by a hood of masonry, continued into a flue of great length, often of a mile, even to three long; this great length being given for the purpose of retaining and economizing the 'lead smoke' produced in working, and at the same time obviating the ill effects of the evolution of a large body of sulphurous acid or anhydride just at the working place. From the front of the hood an iron plate or blower is fixed to lower or raise so as to regulate the draft over the hearth; but for the main draft, which would be deficient in such a long flue, some provision is made in the way of exhausting apparatus, and it also is made to end in a tall upright shaft.

A rich character of ore is usually worked in these hearths, and before actual reduction they are roasted in a reverberatory; and, as in the after reducing operation, only a comparatively low temperature is needed; the lead produced is very pure, from this low temperature being insufficient for the reduction of portions of ores of other metals present, which would vitiate the lead if reduced with it.

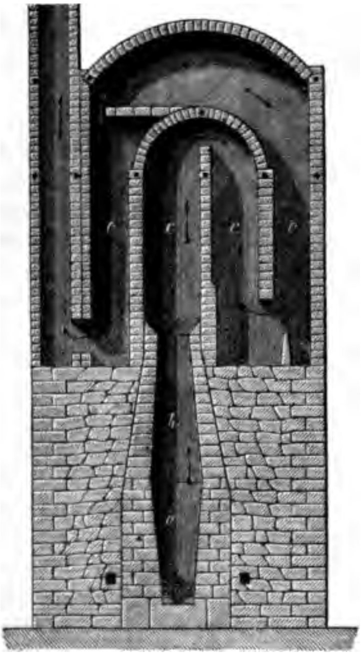
The roasting operation occupies about three hours, a low temperature also is used for this, and frequent stirring, whence the changes effected in the ore are much the same as those already described, viz., the conversion of some sulphide into oxide, and also sulphate by oxidation. The ore, too, thus is rendered spongy and porous, and is therefore drawn out into a tank of water, whence it is removed and dried for the after smelting operation.

The furnace or hearth consists of a rectangular cavity, built in masonry, and lined at the bottom by a thick cast-iron box, the dimensions of which are about 1 foot deep by 21 inches wide, and 23 inches from front to back. The work 'stone'—a sloping plate of iron—is fixed in front of the hearth, and with an inclination from back to front of about 6 inches in 2 feet; it is surrounded by a rim, except on the hearth side. In front of this work-stone a cast-iron pot, for the reception of the reduced metal, is placed; and leading to this from the hearth is a channel hollowed out in the work-stone for the flow of metal down into the pot. At the back of the hearth is a block of cast-iron, called the back-stone: on this the nozzle of the tuyere rests. The back-stone carries a second, placed above, called the pipe-stone, in which latter a cavity for the tuyere is formed. The whole arrangement is completed by side-blocks called bearers and keystones. Lastly, there is a large cross-piece termed a fore-stone. But all are actually heavy masses of iron.

As already stated, before smelting in this furnace, the ore is roasted, unless it contains plumbic carbonate in any quantity. The ore being prepared, for smelting it a quantity of peat is placed in layers in the cavity of the hearth, especially in the front, an ignited peat is then introduced, and a gentle blast turned on so as to ignite the whole; then, to increase the heat, some coal is, if needed, thrown over all. When the heat has been sufficiently got up, some partially fused ore, called browse, and actually a residue of some previous operations, is put on to the fuel; this softens almost at once. The whole is now stirred and drawn forward in portions by a rake, a mass brought out upon the work-stone is examined, and the grey slag with it separated and removed, the richer ore being put back in the furnace. A peat is placed in front of the blast-pipe so as to distribute the blast, and at about every quarter of an hour the charge is examined on the work-stone, and the slag separated; the ore is returned to the hearth; separated lead flowing to the pot; and at the same periods fresh ore and fuel are supplied. During a fourteen hours' working period or 'shift,' from one to two tons of lead will be separated, which is at once cast into pigs from the pot, but a quantity is always put back in the hearth so as to leave it nearly full of lead for the next shift. The separated grey slag retains about one fifteenth of its own weight of lead, and is subsequently smelted in the slag hearth. During working of the ore hearth, if this slag becomes too pasty, the separation of the lead will be hindered; in such case, a little lime is added, to render it less fusible; but, on the other hand, if too refractory, a small portion of lime added will also soften it.

The ore hearth working is really a blast-furnace operation, but at Freiberg where ores are also treated for silver and copper contained with the lead, a true blast-furnace is employed, in which the roasted ores are smelted in conjunction with regulus or slags of other operations. These furnaces are from 20 to 25 feet high, and are blown by ordinary cylinders much on the same plan as those employed in iron blast-furnaces.

Fig. 67.



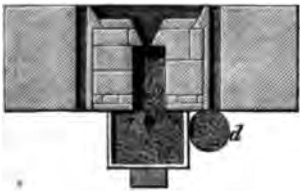


Fig. 68.

Where lead ores are associated with much silica their reduction by ordinary means would be attended with considerable loss, as the plumbic oxide produced would combine with silica, forming a very fusible slag. Hence, such ores are treated with metallic iron, and reduced by the blast-furnace. In the Hartz a peculiar form is so employed, the body, formed by two cones (*a* and *b*), joined at their bases, is about 20 feet high by 3 in diameter at its widest part. The upper part, or mouth, terminates in a set of chambers (*c*), built so as to retard the current from the furnace, and retain the volatilized lead fumes from the charge; these end in a shaft or flue seen on the left, and entered at its lower part. Beneath the furnace body is a cavity (*f*), and in front of this the crucible (*e*), adjacent to, and connected with this, is a second receptacle (*d*) intended also for the reception of the metal and matt which are constantly flowing from the furnace during working. The tuyere for the blast is carried in at the back of the body in such a manner as not to produce oxidation of the charge, but to act on the fuel alone, and for this the charge is introduced at the back, the fuel at the front, and in working, a portion of slag is allowed to solidify round the tuyere so as to blow out into an elongating tube, or 'nose,' which carries the blast forward in the furnace.

The charge consists of 100 parts of ore, and to this is added more than its own weight of scoriæ derived from a previous operation, together with small quantities also of residues, containing a small portion of impure litharge. Then for the reduction from 4 to 5 parts of granulated cast iron is added. During working lead and slag continually flow out together. The slag is composed of some plumbic sulphide mixed with sulphides of other metals present in the ore, and also the iron sulphide resulting from the operation. This slag forms a matt upon the surface of the metal which subsides to the bottom of the second crucible.

The lead is separated and cast into pigs, the matt reserved for a further operation for its reduction. The temperature of the upper part of the furnace is kept as low as possible, to prevent volatilization of the plumbic sulphide of the ore.

In English lead-smelting works, the slags resulting from operations described being, for the most part, poor in lead, require a much higher temperature for the recovery of the metal than that employed in smelting the ore, and for this the slag hearth is most effective. This is a similar apparatus in general arrangement to the blast-furnace (fig. 96), but, as employed for lead ores, the body is very shallow in comparison to its area. It is a rectangular blast chamber, and built in fire material. Its height is from 3 feet to 3 feet 6 inches, by about 1 foot 10 inches wide, and 2 feet 3 inches deep from back to front. At the lower part of the body in front is placed a basin for the reception of the reduced metal, and again in the front of this latter a second one for the exhausted slag. The furnace bottom is covered by an iron plate, and upon this again a thick layer of cinder is packed.

In working, a quantity of fuel is put in (usually peat covered with coke), and after turning on the blast and getting the heat well up, some of the slag is introduced, and as this melts and subsides fresh slag and coke are put in. Upon fusion, reaction of the retained plumbic sulphate takes place upon the plumbic sulphide, which latter is the result of reduction of portions of the sulphate at the high temperature, and again any plumbic oxide present enters also into the reaction. Thus the lead is reduced and set free, but at this high temperature and in presence of carbonaceous matter the small quantities of other metals which were left untouched at the lower temperature at which the first operations were carried on, are now reduced, and mixing with the lead injure its quality. Hence it is sold as 'slag lead.'

The metal which runs into the first basin is allowed to pass from it into a large melting-pot adjacent, whence it is ladled and cast into pigs; the refuse slags pass over the first into a second receptacle, containing cold water, in order to solidify them.

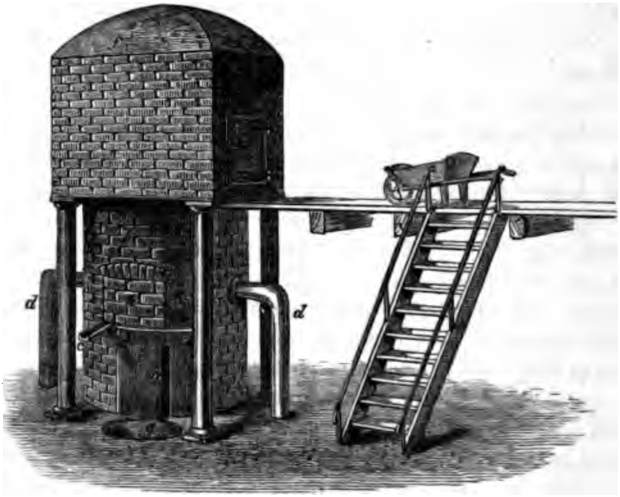


Fig. 69.

The cupola, or Castilian furnace, is applied to the same uses as the slag hearth just described, viz., for smelting refractory ores,

or difficultly reducible slags, as slags from reducing furnaces, also from the lead improving furnaces if they contain silver.

This is a circular blast furnace (fig. 69); internally it is about 8 feet in height, up to the opening (*e*), where the charge is put in, and 2ft. 6in. to 2ft. 10in. diameter. This body (*b*) is of fire-brick, but at the bottom is fitted up to about 3 feet of height, with a brasquing made of fire-lute and ground coke. In the upper part of this a cavity, called the breastpan, is hollowed, so as to retain the smelted metal. At the top of this a spout (*c*) is formed for the outflow of the slag formed during the operation, and at the side of this is a cast-iron plate (*i*), in which a long slot (*a*) is formed, and luted up, but which is tapped from time to time for letting out the reduced metal. This is done by three men, two of whom support the tapping bar by means of two iron bars crossed under it, while the third drives it down the slot by means of a heavy hammer. The metal flows out into the pot (*g*), in front of the furnace, whence it is baled out. Above the cast-iron plate is an opening (*h*) bricked up during the operation; this gives access to the breast pan.

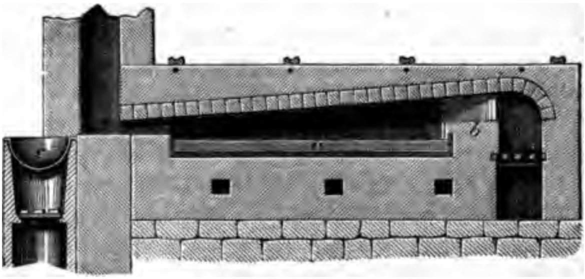
The water tuyeres (*d* and *d*) of a fan-blowing arrangement enter at the sides and back. Four iron pillars carry a square dome or hood, in one side of which is an opening for charging in the material and fuel, which is done by wheeling in by iron barrows.

The material for reduction may contain about 30 per cent of lead, and may be a mixture of ores and slag, which are reduced together. If a flux is needed for the ore, limestone is used. The The charge is put in alternating with layers of fuel (coal or coke). charge is better not too small, or it is liable to stop the draught, and it is damped in order to prevent dust drawing into the flues.

Lead, as obtained from its ores being impure, is in most cases somewhat hard, and requires therefore purification to soften it, or, as it is called, 'improving.' For not only does it contain the silver originally present in the ore, but also antimony, tin, copper, and other impurities; and this is especially the case in leads obtained from Spanish ores.

Softening is performed in a reverberatory built with a very low dome, and whose bed is a large cast-iron pan (*a*), set quite level behind a very broad bridge (*b*). At one end, and a little in front,

Fig. 70.



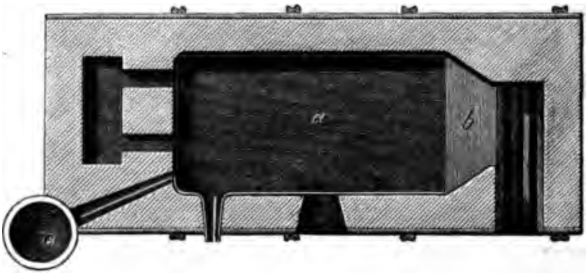


Fig. 71.

is built up a second furnace, provided with an iron melting-pot (*c*). In operating, both fires are lighted, and the pot filled with coarse metal, six or seven tons being generally worked in one operation. In some works no separate melting pot is used, the lead in pigs being charged into the furnace itself and there melted.

A considerable heat is first used, the whole is then cooled; thus a thick pellicle of slag forms; this is raked off, and the heat again raised, and then, on cooling again, more slag is formed and raked, and these operations are repeated until, on examination, the lead is found to be purified; for, ascertaining this, a portion is taken out from time to time and tested. Its surface should now have a peculiar crystalline texture and good blue iridescent colour; if the colour be dull, it is an indication of antimony still present. Again, it should now be quite soft and malleable. The operation being satisfactory, the metal is run into an iron pot and cast into pigs.

Hard leads with much impurity will take fourteen days with constant attention to improve; while some lead needs only twenty-four hours, or even at times less. The slag removed, usually forms on cooling a heavy, hard, brownish mass, but its colour and texture vary according to the nature of the impurities. It is composed of the oxides of antimony, tin, &c., and the former is generally in combination with some oxide of lead, the affinity for which much assists its removal; and during the refining operation, especially if prolonged, a considerable amount of lead oxidizes.

The matters passing out from lead furnaces into their flues have the terms 'lead fume' and 'lead smoke' applied to them; and the condensation and retention of the fume or solid portion is most important, because, in addition to its poisonous nature, if discharged into the air, it occasions loss, at times rising even as high as one seventh of the product, for it consists largely of volatilized lead compounds.

The gaseous constituent of lead smoke is chiefly sulphurous acid (or anhydride), but vapours of arsenious acid (arsenious anhydride) are also commonly evolved. The solid matters are particles of ashes, carbonaceous matter, silica, ferric oxide, &c., carried out of the furnace by the draught. Lastly, the metallic constituents of importance are portions of plumbic sulphide, sulphate, oxide, and carbonate, and generally more or less silver.

Many plans have been proposed for retaining this fume, so as to obviate the expense and care of forming and maintaining long condensing flues, such as condensing it by a shower of water; filtering through very porous solid materials; evolving steam and throwing it in so as to mix with the smoke, &c.; but none seem to be sufficiently effective to set aside the long flue, which is still largely used.

As all lead after reducing retains the amount of silver originally present in the ore, this has now to be removed, which is done by first concentrating the silver into a reduced quantity of lead, and afterwards cupelling this. Formerly, for want of a good and effective process, the lead of commerce always retained a considerable amount of silver, so much as to render its separation a very profitable operation since Mr. Pattinson's process has been in use. That gentleman discovered that if we fuse lead containing any notable amount of silver, and then cool slowly, carefully stirring at the same time, crystals will form in the bath and subside to the bottom; and, moreover, these will be much less rich in silver than the original metal was. Upon this discovery he founded the following operation for removing the poorer lead and concentrating the silver:—

A series of iron pots, from 9 to 11 or 12 in number, are employed. These are hemispherical, of about five feet in diameter, and calculated to hold a charge of about nine tons of metal each. They are set in brick furnaces adjacent to each other, but with quite distinct flues, furnaces, dampers, &c. (fig. 73). Suppose the diagram (fig. 72) to represent the series, and that they are all empty. In it the upper figures represent the pot number, the lower ones the estimated richness of the lead in silver, as usually found resulting in the ordinary course of working the operation.

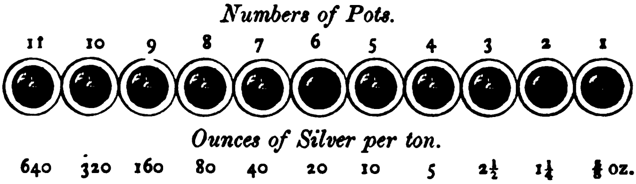


Fig. 72.

Some 10 oz. lead, that is to say, lead containing 10 ozs. of silver per ton, having to be worked, 9 tons of it would be placed in the 5th pot and melted; after complete fusion it is skimmed with a small perforated ladle; thus the fluid lead runs through into the pot, and the dry oxides are reserved for after reduction. The fire is drawn, and the men stir the metal continually; if, however, it is much too hot, they will throw water upon it, which sets the top lead; this they push down with their slices (*e*, fig. 74), but the plan is objectionable for two reasons; first, on account of the danger, as frequently, under some part of the hardened top a certain quantity of water becomes enclosed, and an explosion thence follows; and, secondly, because too much water causes an improper formation of crystals, which retain silver (such crystals are, however, easily distinguished). When the pot begins to thicken from stirring and cooling, one workman takes a crystallizing ladle (*d*, fig. 74). These are large iron ladles of 18 inches diameter by about 5 inches deep; they are perforated at the bottom with half-inch holes, and furnished with very long handles. This handle he raises above his head, sinking the bowl down vertically into the lead until it reaches the bottom; then, by bringing the handle down as far as he is able, he holds it for a companion workman to place a hook, which is attached to a chain over it, and thus, by means of a crab and crane, draws up the

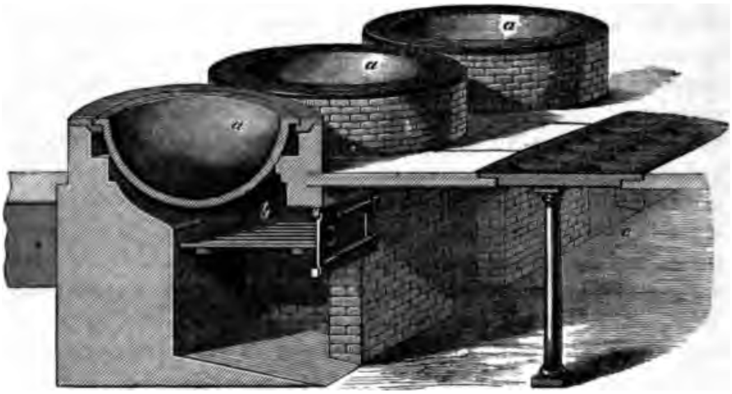


Fig. 73.

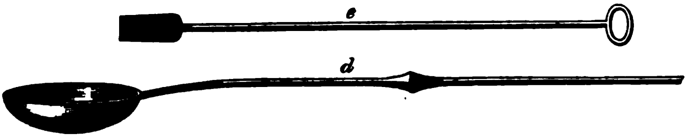


Fig. 74.

ladle full of crystals; the first operator then slides the ladle handle under a shoulder of the crane, and it is left to drain; the second resumes the stirring of the pot, whilst the fluid lead drains out from the holes of the ladle, which is accelerated from time to time by the man in charge of the ladle, who, by shaking the shank, so displaces the crystals as to cause all the fluid lead to run more completely out. This effected, the crane is turned, so as to bring the ladle over pot No. 4, for these crystals are to be turned into it, and will be found to contain only 5 ozs. silver. These operations are continued until ⅔rds of the lead in pot 5 has been passed over in crystals to pot 4, that is to say, six tons out of the nine. Now, under pot 4 a fire is made up, so that the crystals as they are thrown in may be melted. This done, the men with a large plain ladle turn the remaining ⅓rd, or 3 tons of molten lead, in pot 5, and which now contains the remainder of the silver, equalling 20 ozs. per ton, into pot 6.

Now in produce the operation is thus:—In pot 5, nine tons of 10 oz. lead equals 90 ozs. of silver, of which six tons of 5 ozs. or 30 ounces, works into pot 4; and three tons of 20 ozs. or 60 ounces, is ladled into pot 6.

Now, providing there is lead of these two assays in the works, that is, three tons of 5 oz. to add to the six tons passed into pot 4, and also six tons of 20 oz. in the same way, to fill pot 6; this would be done, and both these pots may then be worked at the same time with two different sets of men. Six tons from No. 6 in crystals will work into No. 5, and three tons in bottoms will be put back into the same pot from No. 4, and thus again fill it without any addition of pig lead.

As the lead 'goes up the house' for enrichment it will be found that the separation is not so complete, and in consequence No. 11 pot will not contain as much silver as is specified in the diagram; in order therefore to make the lead more fit for the cupellation process, it is usual, instead of baling out the three tons of bottoms, to continue the stirring in the last working pot until the lead thickens, then drawing this thickened metal round the sides of the pan, a perforated ladle is squeezed down into the centre of it, and held there. Thus a quantity of lead, still fluid from its greater richness, squeezes up into the ladle and is baled out thence by another plain ladle and added to the last pot, by which its silver value is fully brought up to the required estimate.

The rich lead is now finally submitted to cupellation, to separate the silver (see page 169). And as there is generally a loss of about 5 per cent lead in this operation, it is found better to employ lead of this high silver value for it.

During the whole operation much oxidation of the lead is going on, and it is estimated that leads averaging 20 ozs. to the ton will produce a quarter of their weight in 'dross' or oxide to reduce, leads of 30 ozs. about one third; thus 1000 tons a-year of 20 ozs. will give 250 tons to reduce, and the same quantity of 30 oz. about 330 tons.

Reduction of this oxide is accomplished in a reverberatory furnace, having a bed on an inclime towards a tap hole situated on one side at the back end. For the operation the oxides are mixed with some coal of good quality, and a fire then made up in the grate; the reduction is assisted by raking, and the fluid lead allowed to run from the lower part into a pot set outside, and from this it is ladled and cast into pigs, as the pot fills from the reverberatory.

There is another process for desilverizing lead, for which Mr. Parkes obtained patents now about twenty years since. In it he fuses lead and zinc together; subjects the alloy of lead and zinc formed to a liquation process, and then the zinc to distillation, by which the silver is separated with some lead, and finally he recovers the silver by cupelling this lead.

It is well known that lead and zinc will not alloy permanently, but that, on cooling a mixture of the two, the zinc will separate so largely from the lead as to form an upper and distinct layer in the melting pot. But the zinc at the same time removes and retains a small portion of lead, and Parkes found it that it abstracts nearly the whole of any amount of silver originally in the lead.

In his original process he operates by fusing the argentiferous lead in an ordinary Pattinson pot. When melted, fused zinc, in the proportion of about 1 pound up to 1½ pound to the ounce of silver, is ladled in from another pot. The zinc is next stirred into the bath so as to mix it completely with the lead.

Next the fire is lowered carefully to cool down the metal, and as it is at this time that separation of the zinc goes on, and consequently of the silver, attention is needed to effect it properly. It is watched, and, as in Pattinson's operation, any metal setting on the sides of the pot near the surface is broken away into the bath. When zinc begins to solidify on the surface it is skimmed off with a perforated ladle, until removed. The lead is then left for a time further to cool down, and if on examination it is found yet to retain much silver, a second skimming is made for zinc.

When all the solidified zinc is removed, it is liquated in a small iron retort, by which some lead will be separated. After which the former is distilled with a small addition of lime and carbonaceous matter, in some convenient form of zinc retort. Thus the zinc distils over, leaving some lead with which it had alloyed and also the silver with this lead.

The lead is lastly to be cupelled for separation of its silver.

But the original lead will be found hard and unfit for use, for, in addition to any noxious metals which may originally have been present in it, it retains a quantity of zinc, which increases the evil. Therefore it has to be rendered workable by treatment in the improving furnace (page 326). Thus zinc, antimony, any iron, and the like, are oxidized and removed in the ordinary way.

Many improvements have been made upon Parkes' process, and one which deserves especial notice is the use of superheated steam, which amongst other applications is mainly used as an oxidizing agent to the metals retained by the lead. Conduriè has patented this plan of purification. He passes superheated steam for two to three hours into the melted lead. Thus watery vapour is decomposed, furnishing oxygen to the metals to be removed (oxidizing however a small quantity of lead at the same time), the hydrogen set free passes off with the excess of steam.

Percy (*Metallurgy of Lead*, p. 152) states that in examining the results of a working of Parkes' process which he witnessed, the lead left retained 10 dwts. of silver per ton; that liquated retained 55 ozs. per ton; while the zinc skimmed contained 225 ozs. 8 dwts. per ton. The reader who desires the fullest information on Parkes' and Pattinson's processes, will find all he can need in the work just cited.

Although the lead of commerce is very nearly pure, it is never entirely so; consequently, if it be required chemically pure, the best quality of commercial lead must be taken and dissolved in nitric acid, and the resulting nitrate crystallized repeatedly to purify it. This is then heated to redness in a crucible, whereby the nitric acid being decomposed and driven off, a pure oxide of lead remains, which may be reduced to metal by heating with black flux. But it may thus retain traces of silver. If therefore it is to be freed entirely from silver, lead should be dissolved in nitric acid, purified by recrystallization, and then precipitated as sulphate from a dilute solution by sulphuric acid. Thus, dilute, the silver remains untouched. The washed plumbic sulphate is reduced by heating with sodic carbonate and resin in a lined crucible. Or 8 parts of plumbic sulphate may be mixed with 4 of potass and 1 of charcoal, and then reduced at a moderate temperature.

Properties.—When lead is pure it is very soft, and hence may be cut even with the finger-nail, its clean surface being of a bluish white, which rapidly tarnishes from oxidation. Its specific gravity is 11·35. In rolled lead the specific gravity would be increased by condensation of the metal, but such impurities as are found in commercial lead usually lower its specific gravity. It is readily rolled into thin sheets, as it is tolerably malleable and ductile, but it is not very tenacious, although it may be drawn into wire; indeed its tenacity is so low that a wire of ·1 inch diameter will only carry 30 lbs. weight. Lead melts at 617° F. = 325° C., and may be crystallized with care in octohedrons or the primitive form of cubes. I have a very beautiful specimen of lead crystallization in cubes and octohedra. It was given me by Mr. D. C. Griffith, who removed it with some brasque from the interior of a smelting furnace, in which the crystallization had taken place very slowly. If repeatedly heated and fused, it gradually becomes harder, probably from absorption of portions of oxide which become diffused through the mass, for a layer of charcoal put over the metal during fusion will prevent this. It shrinks on cooling, and is not adapted for casts where sharpness is an object.

Pattinson, in attempting to distil lead, found it volatile at very high temperatures, small quantities rising in vapour recondensable into metal. On exposure to heat and air the fume evolved is of plumbous oxide.

Lead is readily acted on by acetic acid, whose vapour corrodes the metal. By cold sulphuric or hydrochloric it is unacted on, and the action is very slight when long boiled with them. In the latter case with sulphuric acid, sulphurous anhydride will be evolved during solution, and with hydrochloric, hydrogen. Nitric acid dissolves it, nitric oxide being evolved, and plumbic nitrate formed. And this acid acts very readily when dilute. Lead, when exposed to the action of pure water containing air, will deposit plumbic oxycarbonate; and the scale of this substance falling off will leave a fresh surface for renewed action, and thus rapid corrosion is the result. Dr. Miller, who, with Mr. Daniell, experimented upon this matter, observed that certain salts, as phosphates, sulphates, and carbonates, diminish the corrosion, while calcic bicarbonate quite hinders it; hence spring waters, which generally contain this substance largely, are inactive upon lead; but chlorides, nitrates, and nitrites, are especially injurious. The quantity in the case of either salt inducing solution is not more than 3 or 4 grains in the gallon.

Water containing carbonic acid to any considerable amount completely dissolves lead, for the plumbic carbonate first formed is readily soluble in excess of carbonic acid, and hence a fresh surface of metal is exposed to action continuously.

If water is boiled so as to expel all air, it is inactive on lead, although the water may be pure. Atomic weight, 207; symbol, Pb''.

Compounds with Oxygen.—There are four in number. The first however being of no great interest. It is a suboxide, having the composition Pb_2O. The second is litharge or plumbic oxide, PbO. Then a peroxide or plumbic dioxide PbO_2. And, fourthly, a compound oxide formed of two proportionals of protoxide with one of dioxide, hence of a composition $2PbO + PbO_2$.

Plumbic oxide, or litharge, is the base of the ordinary lead salts; it is the litharge of commerce, formed on the large scale, by heating lead on an open flat hearth to redness, or above the fusing point of the metal, and removing the oxide as it forms. This is then ground and levigated, whereby the adherent grains of lead are separated and removed. If it is made at a very low temperature, the oxide forms as 'massicot,' a yellow powder; the texture and colour of this depend upon the oxide not having been fused. It is this protoxide which is formed in ordinary cupelling operations, and which, by fusion, is rendered sufficiently liquid as to be capable of absorption by the substance of the cupel. After fusion its colour is of this lemon-yellow hue. It is volatile at a strong red heat, and may be dispersed in fumes. Plumbic oxide may be formed on the small scale, by heating pure plumbic nitrate or carbonate as described in the preparation of pure lead. When pure, it is a lemon-yellow powder; where it inclines to orange or red, it is an evidence of slight admixture of the compound or red oxide with it; but, by heating litharge, this red colour is assumed, which disappears again on cooling. A crystalline hydrated protoxide may be formed by precipitating a plumbic salt by caustic potass, or by dropping a solution of plumbic acetate into ammonia, until the precipitate at first formed becomes permanent. The white powder so obtained may be dried at a gentle heat, and on examination by the microscope will be found to consist of minute transparent four-sided prisms.

Plumbic oxide may be got in a crystalline condition, and anhydrous, by adding ordinary litharge to saturation to a hot solution of caustic soda of about 1·42 S. G. Rose-red crystals are thus deposited as the liquid cools.

Plumbic oxide is the base of ordinary lead salts; it is slightly soluble in water, giving it an alkaline reaction. This reaction is also shown with the subsalts of lead, which this oxide readily forms. The specific gravity of protoxide of lead is 9·3. Composition, Pb O; atomic weight, 223.

Red oxide of lead, or minium, is prepared commercially by heating metallic lead in a reverberatory furnace, keeping the metal constantly stirred, and at a temperature considerably below the melting point of the oxide formed, thus massicot, or plumbic oxide, is first produced. At the end of this operation the charge is raked out and ground fine, having been previously washed from the coarser parts, and from any unoxidized lead. The powder is then again heated and kept at a dull red heat for about 24 hours; the mass being frequently stirred, and the heat not allowed to rise above 600° F. = 315° C. Thus the whole is converted into a brilliant scarlet crystallo-granular powder. The beauty of colour is insured by the large quantity in which it is made for commercial purposes, and yet more by the purity of the lead employed. Thus some of the finest qualities may be produced by employing white lead or plumbic carbonate. Careful heating of this gives, as before stated, a good form of plumbic oxide, which on the necessary second heating affords a fine product of red lead.

Red lead is much used in the manufacture of flint-glass, and as its use is to give transparency to it, it is necessary to have this compound of great purity, for small quantities of other metallic oxides may not only injure the brilliancy of the glass, but also give colour to it, although its transparency is kept up. Thus, in green bottle glass, as an extreme example, the deep colour is entirely due to the large proportion of oxide of iron it contains.

Minium is, as already stated, a mixture of two proportionals of plumbic oxide with one of plumbic dioxide, whence it does not combine with acids; therefore, if we treat it with dilute nitric acid, we are able to dissolve out the plumbic oxide, as it combines with some of the nitric acid, and forms plumbic nitrate, the dioxide at the same time remaining untouched as an insoluble brown powder, which may be washed from the plumbic nitrate and dried.

Plumbic dioxide may be thus prepared, or by fusing litharge with twice its weight of nitre mixed with one quarter its weight of potassic chlorate. Also by acting on minium by chlorine-water, or by heating solution of plumbic acetate with hypochloride of soda or lime.

It is a dark brown powder, and Fremy states that it possesses acid properties, and that by fusion with alkalis salts may be produced, which he has called plumbates. They are, however, very unstable, and are decomposed even by water.

Mixed with a small proportion of sulphur, a compound is produced capable of taking fire upon friction. Hence this oxide is much employed in lucifer-match making.

Plumbic dioxide is insoluble in acids, excepting dilute hydrochloric, and from this it may be again separated by neutralizing with potassa.

Plumbic dioxide is found native at times, and in a crystalline condition in shining hexahedral prisms. It constitutes heavy lead ore. Composition, Pb O_2; atomic weight, 239.

Plumbic chloride is formed when hydrochloric acid, or a soluble chloride, is added to a soluble salt of lead. It falls as a crystalline precipitate, from its sparing solubility in water, one part requiring thirty-three parts of boiling water for its solution. It is fusible into a horny mass like the similar silver salt. This compound is important in connexion with silver assaying. Thus, if a silver under examination by humid assay contain lead, as some of the brittle silvers do, a portion of the salt solution will go to precipitate this chloride, and so a small error of over-estimation of the silver will result. Composition, Pb Cl.; atomic weight, 278.

Plumbic sulphide is found native as galena; but an artificial sulphide is formed by fusing lead and sulphur together in proper proportions, or it may be precipitated as a hydrate, by adding dihydric sulphide to a solution of a lead salt, or even to an insoluble lead compound suspended in water. This hydrate is a black powder.

If plumbic sulphide be acted on by strong nitric acid, or by aqua regia, it is converted into plumbic sulphate, and by the latter solvent some plumbic chloride is also formed at the same time with the sulphate. If dilute nitric acid is used plumbic nitrate is produced, and some sulphur separated in yellow oily beads.

Heated in contact with air, plumbic sulphide is converted into plumbic sulphate, together with some plumbic oxide, some sulphur burning away; but if out of contact with air, and heated to full redness, it is volatile and sublimes without decomposition. Heated with plumbic or with ferric oxide, its lead is reduced, and the sulphur, taking the oxygen of the oxide, escapes as sulphurous acid or anhydride. Heated with metallic iron, lead is reduced, and the sulphur combines with the iron. Composition, Pb S; atomic weight, 239.

Many of our valuable pigments are lead compounds. Thus, ordinary white lead of the painter is plumbic carbonate, and the peculiar body and durability which this gives to oil paint have caused it to be an article of large manufacture. Patent yellow, or Turner's yellow, is a compound of plumbic chloride with plumbic oxide. Chrome yellow is a neutral chromate; and again, when this last is fused with five parts of nitre, plumbic dichromate and potassic chromate are formed. The latter, washed away, leaves the dichromate as a brilliant scarlet powder.

The alloys of lead with the class of metals hitherto considered are not important, as they form in the general brittle unworkable compounds; but they may be enumerated here.

With mercury lead readily amalgamates, either by mixing lead filings with mercury, or by dropping warm mercury into lead in fusion. The resulting amalgam will have a specific gravity above the mean of its constituents, showing that condensation has accompanied the union. Two parts of lead and three of mercury form a solid crystalline amalgam, very white and brittle; with a larger proportion of mercury it will be pasty, or even nearly fluid. In all these amalgams the lead may be partially oxidized by moist air, the oxide formed being a suboxide of lead, which will be mixed with some amalgam as a black powder.

The peculiarities of alloys of lead and silver are taken advantage of in their separation; thus, as has been stated, an alloy rich in silver will remain fluid at a lower temperature than a poor one, the poorer crystallizing out; in fact, the homogeneous alloy of silver thus separating itself under mere management of temperature. Silver thus diffused through a very large quantity of lead will render the latter less malleable. Lastly, if a bar of metallic lead be immersed in a solution of argentic nitrate, the precipitated metal will not be pure silver, but an alloy of silver and lead.

Alloys of gold and lead are brittle in the extreme. Thus Mr. Hatchett found that $\frac{1}{1920}$th of lead in gold will destroy its coining qualities to some extent, by rendering it less ductile. If the amount of alloy in standard gold be formed of lead, and even added to perfectly pure and ductile gold, the colour will be straw-yellow, and the alloy thoroughly brittle. In all cases, however, where gold or silver is alloyed with lead, the latter may be entirely removed by cupellation.

Platinum, with its own weight of lead, forms a purplish white alloy, brittle and granular in structure, and acted upon by the air. The metals have so great an affinity for each other, that a platinum crucible will be perforated by fusing lead in it, or even by oxide of lead, when a reducing flux is used with it; the lead alloying with the metal of the crucible.

Lead cannot be separated from platinum by cupellation as in Deville's process, or even in the small way, without much care; for although, when the lead is in excess, the alloy is very fusible, as the lead oxidizes and the metal becomes richer in platinum, so the fusing point rises, until, at length, the heat of the furnace or muffle is apt to be insufficient, and the alloy sets again, retaining portions of lead.

Palladium and lead form a grey alloy, which is granular in texture, and very hard and brittle.

The more important alloys of lead are those which it forms with tin, antimony, bismuth, and some other metals, constituting the classes of solder, type metal, pewter, &c.: these will be considered in their places.

Discrimination of Lead.—The presence of this metal is indicated by the following tests:—

1st. Dihydric sulphide, or ammonio-hydric sulphide, will throw down a black sulphide from its solutions, insoluble in any excess of the precipitant.

2d. Potash or ammonia throws down hydrated oxide: this is soluble in excess of potassa, but not in ammonia.

3d. Alkaline carbonates precipitate a white plumbic carbonate, which is quickly blackened by dihydric sulphide.

4th. Sulphuric acid is a characteristic test, precipitating a white sulphate: this is also thrown down by any soluble sulphate.

5th. Potassic chromate is also a very delicate and characteristic test, precipitating a fine yellow plumbic chromate, and acting upon exceedingly dilute solutions.

6th. Hydrochloric acid or a chloride gives a white precipitate, soluble in excess of potassa.

7th. A lead salt is readily reduced on a piece of charcoal before the blowpipe, a bead of lead ultimately resulting in the centre of the point of fusion; round which the charcoal will be seen to have absorbed a portion of yellow oxide of lead.

When lead has to be estimated quantitatively it is usually precipitated as plumbic sulphate, and the precipitate washed, dried, and ignited in a porcelain crucible before weighing, the crucible being covered, as plumbic sulphate is slightly volatile.

The solution of the lead salt should be tolerably concentrated, but the acid dilute. Where greater accuracy is needed, about twice the bulk of alcohol is recommended by Fresenius to be added, after which time is given for the subsidence of the precipitate, which, before drying, is to be washed with alcohol, then dried, ignited, and weighed as before.

Lead is sometimes precipitated as sulphide by dihydric sulphide, but before weighing, the precipitate must be dried in a current of hydrogen. If this cannot be done it is better to convert it into sulphate by oxidizing with nitric acid, and weighing it as sulphate.

It is at times weighed as oxide by precipitating by potassa.

The analysis of a silver lead would be performed by solution of the specimen in nitric acid. Then largely dilute, and add a large excess of hydrochloric acid to throw down the silver. Plumbic chloride is prevented from going down by this dilution and excess of acid. Then the lead is precipitated as sulphide, and the latter washed, dried, and weighed, as such, or as sulphate as above directed.

The analysis of a galena for the amount of lead has been given under its assay (p. 315).

CHAPTER XII.

BISMUTH.

This metal has been known for about three centuries, although it is not plentiful, nor are its applications very extensive. It is found principally native, in a matrix of quartz, but it also occurs with sulphur as bismuth glance, a sulphide of the composition $Bi_2 S_3$; at times with oxygen as a sesquioxide; and also in association with lead and copper, in needle ore; sometimes with copper alone, and again with tellurium; and it is generally found to contain silver, and, like lead, may have the latter separated by cupellation. Bismuth is obtained largely at Schneeberg, in Saxony, also in Bohemia and Transylvania. It is also found at Stirling in Scotland, and in England in parts of Cornwall and Cumberland; in the United States, and some other countries.

The metallurgy of bismuth is very simple. The ore is so easily liquated, that the early plan for the separation of the metal was simply to heap the ore upon a floor with the fuel, and apply a steady gentle heat. By this means, it sweated out, and subsided to the bottom of the heap, being found upon the floor at the close of the operation.

At Schneeberg, where much is reduced, the ore contains, together with about 12 per cent of bismuth, a considerable quantity of cobalt also. It is there operated upon in tubular iron retorts, A; these are arranged in a horizontal row of three or four, and inclined from the upper to the lower end, as shown in the section here given. From the upper end the brickwork is gradually bevelled down, towards a trough containing water, D; while below the lower end is placed an iron basin, C. Lastly, above each retort is a couple of holes made through the brickwork of the roof, E E, whereby the draught to each can be increased or diminished at pleasure, by opening or stopping them as required.

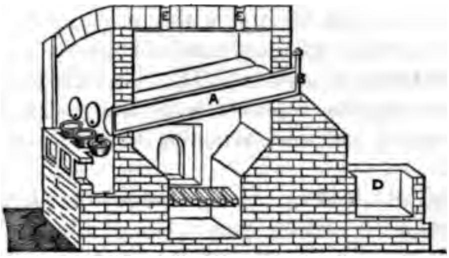


Fig. 75.

In operating, the tubes are charged at their upper ends with about 56 lbs. of native ore. Heat is then applied, and in an already hot furnace, the metal will begin to flow in about ten minutes, at a heat of about 509° F. = 265° C. A small rake is then introduced by the doors at the upper ends, B, and the ore so opened below, as to allow of a free passage of the fluid metal down to the lower end; thence it flows into the iron dishes, where it is protected from the oxidizing action of the air by a covering of powdered charcoal. When the whole of the metal is thus fused out, which will generally be in some 40 minutes, the siliceous residue, with other contained metals, is raked out by the upper door, and allowed to slide down the incline into the water below.

These furnaces are heated at Schneeberg by wood, and a brisk but well-regulated draught kept up during distillation; the holes in the roof serving to direct the current of heat to each retort. Scheerer, however, heats bismuth liquation tubes by means of gas, as a substitute for wood.

Kerl* states that at Joachimsthal, Vogl treats bismuth ores, containing from 10 to 30 per cent of bismuth, in crucibles. He

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[*] Kerl, Handbuch der Metallurgischen hüttenkande, vol. ii. page 827. Crook's Translation, vol. i. page 538.

powders the ore, and mixes it with 28 per cent of iron in small pieces; 15 to 50 per cent of sodic carbonate (the quantity being dependent upon the amount of siliceous gangue), 5 per cent of lime, and 5 of fluor-spar. Crucibles of 23 inches high by about 16 inches diameter, are filled with this mixture, and heated in a wind furnace, stirred, and when fused the contents are ladled out into sugar-loaf-shaped moulds. The bismuth subsides to the bottom of the moulds, together with the speiss, consisting of cobalt and nickel, and also retaining about 2 per cent of the bismuth.

The metal obtained by these processes is not however pure, it generally contains a variable proportion of silver. This may be separated economically by cupellation, just as in the case of silver lead; and the oxide of bismuth decomposed again by a reduction operation. Indeed bismuth cupels so well, that it may be used to substitute lead for that operation upon the small scale.

But the chief impurities of commercial bismuth are sulphur, traces of arsenic, and also of lead and iron. If lead, iron, and silver, are not present, the two former impurities are easily got rid of by simply fusing the bismuth with a little nitre, when they will be oxidized and separated. But, perhaps, in all cases the best method of purification is the following:—

Dissolve the crude metal in nitric acid, and then concentrate the solution by evaporation. Next pour the clear solution into a large bulk of distilled water. It will be thus decomposed, and a white sparkling soluble powder falls, which is a basic nitrate. This is to be removed, and digested for a time in a little caustic potash, whereby any arsenious or arsenic acids present will be dissolved. Next the basic nitrate is to be well washed, dried, and heated with about one-tenth its weight of charcoal in an earthen crucible, thus the salt is reduced, and the bismuth subsides in the pot in a state of purity.

Properties.—Bismuth is of a reddish white colour, hard, and readily broken up, from its crystalline structure. It crystallizes in rhombohedra, nearly approaching the cube, as their angles vary very little from right angles. These may be formed artificially in beautiful masses, by melting a quantity of the metal in a ladle or pot, and after removing it into some glowing coals, or heated sand, allowing the bulk to cool slowly; and in order to prevent the cooling action commencing at the upper surface, the heat of this is kept up by covering the vessel with a shallow iron basin, into which a quantity of hot fuel is placed. As soon as a crust of metal is presumed to have formed round the sides and top, it is pierced at one side by a red-hot iron, and the remaining fluid metal poured out. If then when cold the upper covering be sawn off, the whole interior surface will be found to have crystallized in most regular forms of hollow cubes and tetrahedra.

Bismuth fuses at 507° F. = 264° C., and when added to other metals it lowers their melting points in an extraordinary manner. It volatilizes at a high temperature, and may even be distilled, although with some difficulty. If the metal be exposed at a very high temperature, it burns somewhat like zinc, with a blueish flame, giving off fumes of yellow oxide.

At ordinary temperatures exposure to air does not affect it; but at a red heat it is rapidly oxidized, and hence the crystals formed, as described above, always exhibit a beautiful play of colours, dependent upon the formation of a thin film of oxide, by the agency of the air upon them while still hot. Nitric acid dissolves the metal readily; sulphuric acid only upon boiling; and hydrochloric acid has but little influence on it. Its specific gravity varies from 9·550 to 9·799 according to its condensation. But pressure, instead of increasing its density, on the contrary lowers the specific gravity, no doubt by disintegrating its texture from its crystalline condition. Thus Marchand and Scheerer submitted a cylinder to powerful pressure, and from a specific gravity of 9·799 reduced it to 9·556. It expands largely on cooling after
Bi‴ fusion, viz. to about $\frac{1}{32}$nd of increase in bulk. Its symbol is $\underline{\mathrm{B}'''\mathrm{i}}$; atomic weight, 210.

There are three oxides of bismuth. The first is a sesquioxide, or teroxide, and is the base of the salts of this metal. From this an acid oxide may be prepared, sometimes called bismuthic acid, or bismuthic anhydride; and, lastly, these two oxides unite to form a third; but this latter may perhaps be properly regarded as a salt, wherein an atom of sesquioxide, $B_2 O_3$, is united as base, with an atom of bismuthic acid, $B_2 O_5$, as the acid of the combination. Its composition is thus, $Bi_2 O_4$.

The ordinary oxide of bismuth of commerce, or sesquioxide, may be prepared in the dry way, by heating the basic nitrate (as formed for the preparation of pure bismuth) in a porcelain crucible to a low red heat; thus the nitric acid is driven off, and a yellow powder remains, which is anhydrous sesquioxide.

In the hydrated state this oxide is a white powder, and may be obtained by the addition of ammonia in excess to a soluble salt of bismuth. The composition of the anhydrous oxide is $Bi_2 O_3$, and its atomic weight 468. In the hydrous oxide this is in combination with one proportional of water. It is then $Bi_2 O_3, H_2 O$.

Bismuthic chloride is obtained as a deliquescent solid, by distilling two parts of mercuric chloride with one of bismuth in powder. It is volatile and fusible, and if thrown into water it decomposes, and the result is an oxychloride of bismuth with hydrochloric acid. This oxychloride has long been known under the name of pearl white. The composition of bismuthic chloride is $Bi Cl_3$; atomic weight, 316·5.

There is a sulphide corresponding to the sesquioxide. It is thrown down when we treat a solution of bismuth with dihydric sulphide, or ammonio-hydric sulphide; this precipitate when washed and dried is a black powder. But the sulphide may be formed by fusing the proportions of sulphur and bismuth together in a covered crucible; thus prepared it is a metallic-looking solid of a dark grey colour. Composition, $Bi_2 S_3$; atomic weight, 516.

Alloys.—Bismuth readily amalgamates with mercury. Thus, if bismuth is fused, and then twice its weight of hot mercury be added, a pasty amalgam is obtained, which after a time becomes granular, harder, and partly crystalline. Gmelin states that as a small quantity of bismuth diminishes the fluidity of mercury very slightly, it is used to adulterate the latter; but the adulteration may be detected by shaking the mercury with air, when a black powder will speedily separate.

Bismuth and silver when fused together in equal parts form an alloy tending to the red colour of bismuth. It is very brittle and scaly in texture, and may be cupelled, whereby the whole of the bismuth will be separated by oxidation, and a mass of pure silver left. Bismuth may in like manner be separated from its alloy with gold.

Bismuth may be alloyed with platinum, and also with palladium. The metals being readily fused together. In the former case one part of platinum may be combined with two of bismuth, and for this it is better to use finely divided or sponge platinum. Palladium may be combined with its own weight of bismuth. In both the alloy is grey, brittle, and easily fusible.

Bismuth when alloyed with lead produces an alloy of greater density than the mean; and if the former be added in small quantity only, the lead is rendered more tough, but without becoming brittle; but if the two are combined in equal proportions, the alloy has the properties of bismuth, viz., it is reddish in colour, and brittle and laminar in texture.

The alloys of bismuth, formed with lead and tin, constituting fusible metal and some kinds of solders, &c., are the more important ones, and will be described under the article Tin.

Detection of Bismuth.—The salts of this metal are for the most part devoid of colour, some are soluble, others insoluble, the soluble salts redden litmus paper; and when the water is in considerable quantity, and contains but little free acid, they are decomposed and deposit more or less soluble basic or subsalts. In the case of the basic nitrate so formed, it is slightly soluble, but the basic chloride, on the other hand, is quite insoluble. The above property of forming subsalts is very characteristic.

Dihydric sulphide, or ammonio-hydric sulphide, throws down a black sulphide, insoluble in excess of these precipitants. This sulphide is decomposed, and dissolved by strong boiling nitric acid.

The alkalis, potash, soda, or ammonia, throw down white hydrated oxide. Upon boiling this precipitate, it becomes yellow. Potassic chromate throws down a yellow chromate of bismuth, form a third; but this latter may perhaps be properly regarded as a salt, wherein an atom of sesquioxide, $B_2 O_3$, is united as base, with an atom of bismuthic acid, $B_2 O_5$, as the acid of the combination. Its composition is thus, $Bi_2 O_4$.

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The metals, lead, tin, copper, iron, or muth in the metallic state. And, lastly, bismuth with sodic carbonate in the blow get a bead of the metal, surrounded by a This may again be distinguished from lea the bead under the hammer. The yello oxide, and is of a deep orange colour while h

Estimation of Bismuth.—This is commo precipitation being first effected by an alka of ammonia, the bismuth compound havi solution in nitric acid; for this precipitant to a hydrochloric solution of the metal. I solution, it must be first precipitated by the bismuthic sulphide separated and ox strong nitric acid. The solution is diluted been slightly acidulated with acetic or nit the precipitation as carbonate is effected excess of ammonic carbonate, then heati after which the precipitate is separated an a porcelain crucible. When the precipitate it is quite converted into sesquioxide, and 89·74 per cent of the whole will be metal.

In precipitating a bismuth solution by water containing a litt and then precipitate by ammonio-hydric sulphide. In either case the sulphide cannot be weighed to obtain a correct result, as it is apt to contain free sulphur, consequently the filter and its contained sulphide are treated in a beaker with moderately strong nitric acid and heating, as already described.

To ensure complete precipitation of bismuth by ammonic sesqui-carbonate, the beaker containing the solution must stand exposed to the air for three or four hours in a warm place, because on the first addition of the ammonia salt, some of the bismuthic carbonate formed is re-dissolved, but by this exposure it will again completely separate.

The analysis of a mixture of bismuth and lead is made by dissolving the alloy in nitric acid. Then on adding to this an excess of caustic potassa, the oxides of lead and bismuth will be precipitated, but the lead oxide is at once re-dissolved by the alkali. The bismuth oxide is to be filtered out, washed, ignited, and weighed.

The filtrate, containing the lead, may next be treated with excess of dihydric sulphide, and the lead sulphide converted into sulphate, as described at page 340.

The method just given may serve where very close accuracy is not required, but for closer results a good method is given by Ullgren. He precipitates the two metals as carbonates, and re-dissolves these in acetic acid. Next, a plate of clean lead is carefully weighed, and then immersed completely in the solution, which is to be covered up, and allowed to stand for some hours. When all the bismuth has been thrown down in the metallic state, the lead plate is to be again carefully weighed. Next dissolve the precipitated bismuth in nitric acid, and re-precipitate by ammonic sesqui-carbonate, as already described for its estimation.

Lastly, from the acetic solution throw down the lead by ammonic sesqui-carbonate. Dry, ignite, and weigh as lead oxide, but from this must be deducted an amount of oxide corresponding to the metallic lead which was dissolved in precipitating the bismuth; the remainder is the weight corresponding to the lead in the sample under analysis.

The analysis of an alloy of bismuth and copper may be made as follows:—The solution of a weighed quantity being effected in nitric acid, and any great excess of the latter neutralized by ammonia, a considerable quantity of sodic chloride is added, and after it a large bulk of water. Let it stand till clear, and then test with a little more water whether any turbidity is produced by it; if so, add water till all the bismuth is thrown down as basic chloride. Next separate it, wash and dry, and then reduce it by potassic cyanide, for which purpose the precipitate is fused in a porcelain crucible with about five times its weight of the latter. From the cooled fused mass, the grains of bismuth are separated by treatment with water; they are then quickly washed, first with water, and next with alcohol, dried and weighed.

The copper may then be precipitated by dihydric sulphide, and estimated as directed in the article upon Copper. The analysis of 'fusible metals' will be given after the consideration of Cadmium and Tin.

CHAPTER XIII.

COPPER.

ALTHOUGH ores of copper were probably as early, or earlier known than those of any other metal, it is likely that the production of the true metal is an operation of comparatively recent date, and that in the smelting of ancient times zinc or its ores were associated with the copper ores, and so the product was actually brass, or, in some cases bronze, where any tin was employed. Thus, in the Bible, we read of 'a land out of whose hills thou mayest dig brass.'

Cornwall and Swansea are now the great producing localities of this metal, but much ore is sent from Australia as rich carbonates, containing, on an average, about 30 per cent of copper. North America, Siberia, and the Ural district furnish copper; the two former largely as native copper, the latter as a subsulphide. Ores from Chili and Cuba are also brought to Swansea for smelting; and, lastly, Saxony and Spain furnish copper ores.

The ores of copper are as follows:—

1st. Native copper, found at times in immense masses, so that we have authentic accounts of large flattened masses being found in the neighbourhood of Lake Superior (N. America), of 14 to 18 cwt. in weight. A broad, thin, and compact piece of 14 cwt. is described as 42 inches long by 30 broad and 8 thick, and having its surface covered with specks of silver. Phillips states that masses of no less than 150 tons weight have been found here; and there is a record of one found at Minnesota in 1854, which weighed 500 tons. Native copper is also found in considerable quantity in Peru and Chili as copper sand or barilla, mixed with quartzose sand, but averaging as much as 80 per cent copper.

Native copper in America is found in alluvial soils; and it is now a received opinion that these masses, which, like gold nuggets, have all the appearance of having been at some time in fusion, may rather have been formed by electro-chemical agency, the cupric sulphide on exposure to moist air becoming sulphate, which by this electric decomposition is reduced to the reguline state.

2nd. The most common of all copper ores is perhaps the ordinary copper pyrites, the German Kupferkies, from which five-sixths of the copper in Great Britain are obtained. This is a natural combination of the sulphides of copper and iron, having usually the composition $Cu_2 S, Fe_2 S_3$. It should contain 34·4 per cent copper. But in the general its average of copper is 12 per cent, down even to 6. It contains a considerable percentage of arsenical pyrites, and also of stannic oxide. It has a brassy colour, and an average specific gravity of 4·2. It occurs in primitive rocks, and especially in clay slate.

3rd. A sulphide called purple copper, or variegated ore, the German Buntkupfererz. This has the formula $3\ Cu_2 S, Fe_2 S_3$, and contains 56 per cent copper.

4th. Subsulphide, or copper glance, $Cu_2 S = 79$ per cent copper.

5th. Indigo copper ore found in Chili, $Cu S$; this contains 66 per cent copper.

With these sulphides may be mentioned, although it can hardly be called an ore of copper, silver copper glance. This is found in Siberia. It is $Cu_2 S + Ag S$, and contains as much as 53 per cent silver, with 31 of copper.

6th. Grey copper, or German Fahlerz, is of a grey colour, and valuable from the silver it contains. It should contain about 48 per cent copper. But this varies much, as it is associated with varying quantities of antimony, arsenic, zinc, and iron. It occasionally contains gold, and more rarely platinum. The amount of silver also is very variable. S. G. 4·6 to 6·0.

7th. The blue and green carbonates are the ores of Australia, and the beautiful Russian mineral known as malachite is a green carbonate. This has a composition Cu O, H_2 O, Cu Co_3, and contains 57 per cent copper; its specific gravity is 3·5 to 4·0. As well as in South Australia, it is found largely in the Ural; also in South America.

The blue carbonate, which is sometimes called Azurite, or Chessylite (from Chessy, in Bohemia) has the formula Cu O,
$2 CuCo_3$ H_2 O, 2 Cu $_{\wedge}O_3$. It contains 55 per cent copper; specific gravity, 3·2 to 3·6.

8th. Silicate of copper occurs in large quantities in the Ural.

9th. Red and black oxides are found; the first, containing 88, and the latter 80 per cent copper.

About 35 per cent of all British copper is supplied by the mines of Cornwall, but the great smelting-works are at Swansea. Indeed, out of nineteen in operation in this country, seventeen are situated at Swansea; and so extensive are these, that the atmosphere for some miles round is thoroughly impregnated with the noxious fumes evolved. They produce annually near 20,000 tons of copper.

Previous to smelting an ore, it is most important to have a correct assay of its value; and for this purpose, although many excellent wet methods have been devised as substitutes for the dry, because this, although simple, is a tedious operation, requiring much experience in the practice; yet smelters prefer and retain the latter as more assimilating the after actual reducing operations upon the ore.

The Cornish method is practised in a small wind furnace, sometimes made with a fire body of sufficient size to work four crucibles at one operation; but the work is performed by several stages.

The quantity of ore taken is determined by its richness, and varies from one to four hundred grains in weight. It is previously powdered, and sometimes has a preliminary roasting. A weighed quantity is mixed with about twice its weight of a flux composed of about equal weights of lime, borax, powdered glass, and calcic

the mixed mass composed of the regulus of
sided under a layer of slag, is plunged into
the glassy slag is cracked and rendered ea
done (with care, not to lose any of the britt
powdered and then roasted, so as further
contents. For this it is carefully kept fr
evolution assisted by stirring during the
operation.

When the roasting is completed, the r
crucible, mixed with a flux composed of ar
The crucible is then heated until the coppe
slag formed.

Lastly, the button of coarse metal is sepa
throwing it into a red-hot crucible, and th
quantity of white flux.

Again, after separating from the slag, th
weighing, and the amount of copper is thus as

The first or roasting operation occupies
20 minutes; the roasting of the regulus, a q
20 minutes; the reduction, another 10 to 1
refining, 5 to 10 minutes.

There are several good wet methods o
First of these, Parkes employs a solution of
having the property of decolorizing any solu
nsely blue by the addition of

potassic cyanide to the 1000 of water; and of this, which is somewhat stronger, about 950 grains, equal 10 of copper.

In testing it, this weight of pure copper is dissolved in a small quantity of nitric acid in a 20-oz. flask; and when nitrous fumes are all driven out by heating after action has ceased, water is added so as about to half-fill the flask. Next an excess of ammonia solution, and then the whole allowed to cool.

A Mohr's burette, graduated to contain 1000 grains in 5-grain divisions (or 100 cubic centimetres, proportionally divided may be used), and fitted either with a glass cock formed in the tube, or with a piece of caoutchouc tube for closing by an ordinary pinch-cock, is filled with the cyanide solution to its zero line. The whole is mounted, so as to allow of the assay-flask being brought under its tip. The solution is now run in by degrees, observing between each addition the decrease of colour, and at last working cautiously until a point is arrived at when the blue has *very nearly* disappeared. It is then allowed to stand, when, in about half an hour, all tint of blue will have disappeared, and the whole will be colourless. The amount of cyanide used is now observed, and its decolorizing value noted; but this should always be determined by taking the mean of two or three of these trials.

The actual assay is carried out in precisely similar manner, modified, however, by the presence of gangue, and associated metals in the ore.

The weighed portion for assay is put into a small flask, moistened with a little sulphuric acid, and then treated with sufficient strong nitric for solution. When action ceases, and fumes are no longer evolved, it is diluted and heated up again; after which the solution is poured into the large assay-flask, the residual gangue washed, and the washings added, and the whole quantity made up to about 10 to 15 ounces. Excess of ammonia is then added; this precipitates a quantity of hydrated oxide of iron, and as this is very retentive of the fluid in which it is precipitated, it is allowed to remain in the solution during the assay, for if filtered out it would retain much copper solution.

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grains of solution, and that of
required in this assay of ore. The
then got at by a simple question o

As 940 : 600 : :

Silver, zinc, cobalt, and nicke
silver is, however, easily removed b
filtering out the chloride.

The cyanide solution is somew
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it is very permanent.

For full details upon this and t
is referred to Percy's *Metallurgy*,
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means of standard solutions at pr
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other methods, it requires to be skil

In Pelouze's method he employ
one of disodic sulphide. The co
Parkes's, and ammonia added, and
is kept at a boiling temperature, a
time till complete.

next potassic iodide, both in excess. In this way the copper is converted into a subiodide, and some iodine is set free; when a few drops of starch added will colour this deep blue.

The estimation is then made by ascertaining the quantity of iodine so set free, by means of a standard solution of sodic hyposulphite, which, by oxidizing the iodine, destroys the blue tinge it has derived from the starch. This standard solution is made and verified by a known weight of some pure copper, treated in the same way as in the ore operations subsequently to be carried out.

Reduction of Metallic Copper from its Ores.—Of the several processes that carried on at Swansea may be first described as most important. The principal ore worked there is copper pyrites, but other and richer ores are worked in, and reduced at fit stages of the operation. The calcining operations to which the ore is subjected, not only drive off much sulphur and volatile impurities, but they have the effect of oxidizing the iron, which has a much greater affinity for oxygen than the copper has; and further, in presence of siliceous matters, this oxidation is yet more readily effected, the iron oxide with them producing scoriæ, which separate from the matts formed, and leave the latter richer in copper just in proportion as the iron is thus withdrawn. These operations are carried on, the copper retaining its sulphur, while the iron is separated by degrees. At last the copper sulphide is partly reduced, copper disulphide being formed, and then some copper becoming oxidized, they react on each other, and impure or blistered copper is reduced, which, by refining operations, has its remaining impurities separated and is rendered malleable.

The first calcining operation upon the ore is performed in a large reverberatory furnace whose bed is formed by refractory bricks set in fire-clay, and large enough to contain about three tons of ore, the bed being about 16 ft. by 13 ft. 6 inches. The fuel used at Swansea is anthracite coal, but mixed with about a quarter of its weight of some bituminous coal, and the supply of air is so regulated, as that the carbonic oxide formed during combustion shall itself be burned in passing over the ore, and thus afford the flame needed.

The ore is wheeled on to the top of the crown or arch in barrows, and then thrown in by the hoppers, A A, after which it is raked evenly over the bed. The fire is next raised to a moderate temperature, and then maintained at this for some eight hours or more, care being used that it is not sufficiently high to fuse the surface, and so, by caking the mass, stop the evolution of volatile matters. At the end of two hours, during which much watery vapour and sulphurous anhydride are given off, the surface is furrowed afresh; and this is done every two hours, and fresh fuel added, until as much of the volatile matters as possible has been dissipated. For this object twelve hours will generally be requisite, when the fire is urged, and afterwards the doors in the bed opened, and the charge raked into the vault, B — a most unwholesome operation, the workmen being exposed to sulphurous and often arsenical vapours. The furnace is not allowed to cool down, but a fresh charge introduced at once.

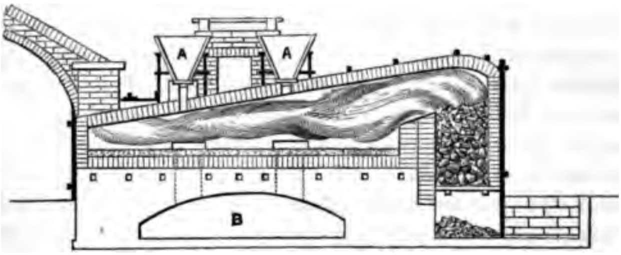

Fig. 76.

The noxious eliminations which throughout the whole calcination are passing from the furnace are chiefly arsenical vapours and sulphurous anhydride, but there are also volatile fluorine compounds, together with carbonic acid and watery vapour given off. In consequence of the injurious character of these fumes upon surrounding vegetation, &c., many plans have been devised for condensing or diffusing them by long shafts, condensing chambers, &c., but many have been tried and set aside. Of late, however, the sulphur separated from the ore as sulphurous anhydride has been doubly utilized. First, by the sulphur being so burned as to serve as so much fuel for the calcining operation; and, secondly, by being brought into the condition of sulphurous acid, it is next carried into leaden chambers, and there converted into sulphuric. For this, Gerstenhöfer has devised a furnace wherein the coarsely powdered ore is passed into it continuously, and comes in contact with bricks heated to a temperature sufficient to inflame the sulphur, the necessary air being thrown in also in a heated state. The evolved sulphurous acid being subsequently converted, as above stated, into sulphuric.

The second operation is performed in a somewhat similar furnace, called the ore furnace. The object is to separate the iron (which has been oxidized in the calcining operation) as a silicate, and convert the copper into a disulphide, containing some oxide of copper. If the ore contained a sufficient quantity of silica, it would be used alone, otherwise some slag of other operations is

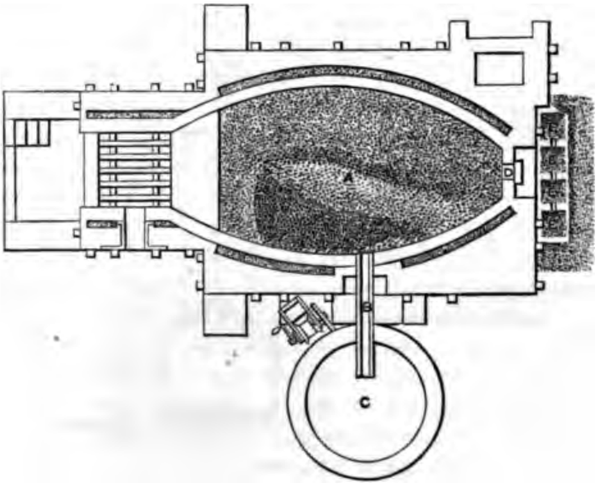

Fig. 77.

added to furnish what is required. Also, a small proportion of other crude ores, such as oxides or carbonates which are tolerably free from sulphides. A mixture is thus made of about seventeen hundredweight of calcined ore, with two and a half of slags, with some fluor spar added; next, three and a half of slags derived from some of the accessory operations named, and three hundredweight of the above crude ores. In all, a charge of little more than a ton and a quarter.

The bed, A, of the ore furnace (fig. 77) is formed into a deep deperssion at one side, from which a channel, B, flows to a water-tank, C. This latter is provided with a cage and windlass for raising the matters sunk in it. At the back is an opening, D, for working the charge, and allowing the slag to flow out into the moulds, E E E E.

A side view of this furnace is here given, showing the granulating tank and apparatus for retaining and raising the matt. It is about one-third the size of the calciner.

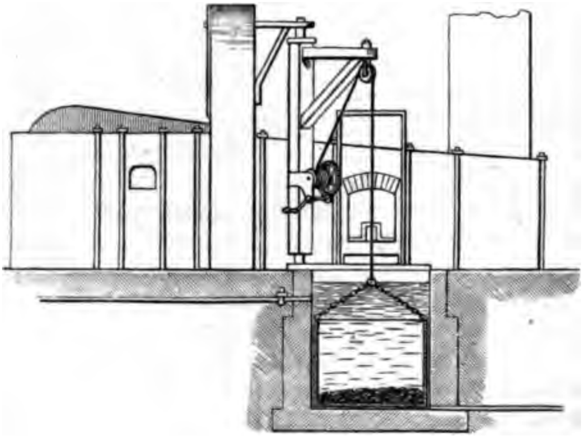

Fig. 78.

The ore being charged in, it is gradually heated for about three hours and a half, till fusion commences. The heat is maintained for another half-hour, after which the furnace man stirs the materials and rakes any unfused portions into the general mass. As fusion progresses, it is agitated by the escape of sulphurous anhydride due to the decomposition of the remaining sulphide of iron, which latter, by taking oxygen and silica, forms ferrous silicate. Any cupric oxide present in the ore would similarly have a tendency to combine with silica and pass into slags, but for the presence of this sulphide of iron, which takes the oxygen needed from the cupric oxide, the latter entering into the condition of sulphide at the same time, by means of sulphur derived from the iron sulphide.

The fire is now urged to get the charge well liquid, so that the matt formed may subside through the slag; then, at the end of about five hours altogether, the tap-hole is opened, and the matt or fused 'coarse metal' allowed to flow into the tank, by which it is granulated. Next, the slag is drawn out into the moulds placed at the back, and any copper contained in this slag subsides and collects at the bottom; hence the cakes, on being removed from the moulds, are broken so as to separate the actual slag, the metal so recovered being added to that raised from the tank. The slag is chiefly silicate of iron, and the chemical changes of this operation consist mainly in the formation of this, with accompanying evolution of sulphurous and sulphuric acids. The matt contains about 33 per cent copper.

After the first or calcining operation upon the ore, the products of all others are termed 'metal,' but it is not until the completion of the fifth has been carried out that the copper is free from other elements, and really metallic. The matt of granulated 'coarse metal' is next raised from the tank and dried; and a third operation is now commenced, in a furnace very much resembling the calcining one. It consists in roasting the granulated coarse metal for a period of twenty-four to thirty-six hours, at a high temperature, commencing with a moderate one, and gradually raising it so as not to fuse the charge. More sulphur is thus got rid of, and some of the iron sulphide oxidized, which is easily effected now that much of the earthy matters is removed from the materials in the form of slag. About three tons are operated upon, and it is raked every two hours or so; and this is a part of the work needing to be carefully carried out, in order to ensure decomposition of the sulphur compounds.

The operation completed, the product will be a compact, blackish, friable mass, called 'calcined coarse metal,' and consisting of sulphide of copper, oxide of iron, and some yet unchanged sulphide of iron remaining.

The fourth operation is for the conversion of this into 'white or fine metal.' For this the last product is mixed with rich ore, containing sulphide and oxide of copper and silica, with but little sulphide of iron. The object is to remove the remaining sulphide of iron by converting it into oxide, for which purpose the oxide of copper in the added ores furnishes oxygen, and the silica then combining with this oxide of iron a slag of silicate of iron results, and at the same time the whole of the copper becomes cupreous sulphide, or $Cu_2 S$. A furnace very similar to the second one is used, but with a flat bed sloping towards a tap-hole. The charge of a little more than 1½ ton is mixed, as above stated, to which are added some scoriæ from the fifth and sixth, or refining operation, proportioned according to the judgment of the operator. If correct in these proportions, the resulting product will be 'white metal.' Should he have used a deficient quantity of oxidized copper compounds, the product will retain a quantity of iron, and is then called, from its colour, 'blue metal.' If, on the other hand, he has had an excess of them, some copper will be reduced, and the product will be reddish in colour, and covered with small elevations, caused by the evolution of sulphurous anhydride. In this latter case the product will be 'pimple metal.'

The mixture having been made as before stated, it is spread over the bed of the furnace. The doors are well closed, and fusion commences in about an hour, and in from three to four hours the whole is rabbled, and the unfused portions stirred into the bath. The heat is raised so as to bring the whole into a thoroughly liquid state, and at the end of about six hours the reaction will be completed. The tap-hole is now opened, the charge run out, and the matt so obtained cast into pigs. These (if the four operations have been well carried out) will contain, in 100 parts, Cu 73, Fe 6·5, S 20·5. The richer portion of them is contained on the upper part of the pig, and is sometimes sold as 'best selected copper' at the market sales.

The scoriæ or slag flows out after the matt; this is chiefly silicate of iron, but retaining some copper which has to be recovered.

The next four operations have been mentioned as collateral ones, for they are not practised upon the product last described, but upon the slags collected, to which rich foreign ores are frequently added; the details of these may therefore be passed over.

The fifth operation (if we do not enumerate the above four) is for the purpose of getting rid of the sulphur, and producing 'blistered copper.' Some 3½ tons of pigs are piled upon the bed of a reverberatory furnace, the openings closed, and quick fire got up, to which the matt is exposed for about four hours. At first both the surface copper and sulphur of the metallic mass are oxidized; and it is now one object of the operation to get a portion of the copper converted into oxide; when it is effected the heat is raised, and now after a time the pigs fuse, and then a most violent reaction of oxide of copper upon the sulphide takes place, and the molten mass quite boils from the evolution of sulphurous anhydride, formed by union of the oxygen with the sulphur, the heat is therefore lowered, and the metal left to itself for a while, in order to give time for the reaction taking place. A crust forms upon the surface, and this swelling and bursting, to allow of the escape of gases, which goes on for some ten or twelve hours, stirs and breaks up the charge spontaneously, and much better than it could be effected by any mechanical means. Evolution of gas ceasing, the fire is again urged to a brisk red heat, when it will be again set up, and at the expiration of a further six hours or so the chief part of it will have been driven off; the heat is then raised to the highest, and the fusion of the whole mass, effected by this, brings about the union of the remaining metallic oxides with silica, but at the same time any oxide of copper remaining undecomposed is also lost to the present product, by uniting with silica; but it thus forms a scoria or slag, which is retained, and worked for recovery of this metal as part of the charge in the fourth operation. The tap-hole of the furnace is then opened, and the reduced copper run off from the silicates, which are left as slags. The copper, running into moulds, constitutes blistered copper, so called from the cavities which it exhibits on fracture; its colour is of a deep red, due to the presence of small amounts of retained impurities, as traces of sulphur, arsenic, iron, and some other metallic matters; hence it is wanting in tenacity, and requires yet a final operation for its refining.

In refining or toughening copper, a charge of about eight tons is operated upon at once, the process being carried out in a reverberatory having a large grate, so as to allow of the use of a very large body of fuel. By means of a tool resembling a baker's 'peel,' the ingots of blistered copper are introduced into the body of the furnace, and they are arranged in such a manner as to expose as much as possible of their surface to the action of the flame, as also to admit of free circulation of air over them, and in order to prolong this atmospheric action upon them while in the solid condition the heat is kept at a moderate degree, their somewhat porous condition allowing of oxidation of impurities taking place in the substance of the ingots. After about six hours of this roasting the heat is raised and the metal begins to melt, and, when melted, a quantity of oxide of copper is formed, which will be partly diffused through the melted mass, while another part will go to oxidize any iron which may chance to be still remaining in it. The evidence of the presence of oxide still in the metal is afforded by taking out a portion, and, when cool, breaking it, when it will be found to be still of a very coarse brittle texture, and its bright red colour very much darkened by the oxide, and the copper is thus said to be 'dry.' From examination of the copper in this condition the refiner judges of the amount of poling needed to bring the metal to 'tough pitch.' After about eighteen hours, any oxides remaining will have united with the silica furnished by the sand adherent to the ingots. The heat is then kept up for some two or three hours longer; after which the scoriæ are raked off the bath, and the metal is said to be ready for refining. The separated scoriæ are worked again to separate any copper, and in the fourth operation. The refining operation, having for its object the reduction of the diffused oxide of copper above mentioned, is effected as follows:—

The surface of the bath is first covered with powdered charcoal or anthracite, so as to protect it as much as possible from the action of the air, and at the same time to furnish material for the withdrawal of oxygen. Next, in order to bring all the metal under the influence of the carbon, it is vigorously stirred with poles of green birch-wood, the fire at the same time being shut off from it. This is a very old practice, but one which has not hitherto been superseded; it is called poling.

The evolution of carbonaceous gases, upon stirring the melted mass with these, reduces any oxide of copper in their passage through the bath; indeed, the first effect of the introduction of the poles into it, is to produce a violent commotion in the molten matter, and this is kept up some 25 minutes, the charcoal powder or anthracite being at the same time supplied as it burns away.

But the duration of this work is determined by constant trials of the metal during its progress being made by the assayer. When he finds that the product is satisfactory as to colour, fracture, &c., he directly stops the poling, or the product would be deteriorated by it; the metal would become what is called 'over-poled.' The examination is made by taking out a small ingot-mould or ladle full of metal, and plunging it suddenly in water; a cut surface is then made, in which a fibrous grain should be perceptible, and the colour should be brilliant, with a silky lustre; at the same time its brittleness is tested by bending.

The effect of over- will be the same as under-poling, as far as regards the application and use of the metal, for in both cases it will be harsh and brittle; indeed, even more so in over-poled metal. For in under-poled, the evils have been stated to depend upon the presence of oxide remaining, and in over-poled, on carbide of copper being formed. But it is now considered, instead of these, to result from the great difficulty of removing the last traces of impurity by ordinary refining, and, therefore, a small quantity of oxygen remaining prevents their alloying or combining with the copper, and the metal will be really over-poled when this oxygen is all separated. If this last state has been arrived at, the remedy consists in skimming off all the charcoal, and exposing the melted metal to a current of air passed through the furnace, again stopping this when the proper state of texture has been arrived at, by the absorption of the requisite oxygen.

The poling properly performed, the fire is again renewed, the scoriæ removed, and a few shovelsful of charcoal thrown afresh over the surface. Lastly, the copper is dipped out by means of clay-coated ladles, and cast into ingots.

By examination of a great number of specimens of refined coppers, Abel and Field have shown that in all some impurities are retained. They state that arsenic and silver are almost invariably present, bismuth very generally, antimony not very commonly, lead always present in sheet or rod copper, but rare in cake. Iron is almost entirely removed by the refining operation. Of non-metallic elements, sulphur is also only found in minute traces, some oxygen is present generally, and in some cases selenium.*

The presence of lead may be accounted for, from its being a general practice to scorify copper while in the refinery (as a last operation) with lead. It has already been stated that plumbic oxide, as formed in cupelling operations, acts as a carrier of oxygen to other metals for their separation. For this same end about half a per cent of lead is added to the yet molten copper, and well stirred into it. It becomes oxidized by the air, but takes also oxygen from the copper. It then affords oxygen to any arsenic, iron, antimony, or other base metals present, which will thus be separated as scoriæ with the plumbic oxide. Lastly, the lead is carefully and completely separated from the copper as thoroughly as possible, for any retained would be injurious to it; this is effected by constant stirring, so as to bring it under the oxidizing influence of the air, the oxide formed being cleanly raked off the surface of the bath before casting.

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* Some excellent papers by Abel and by F. Field upon the analysis and impurities of commercial copper will be found in the *Journal of the Chemical Society* for 1862 and 1864.

The process of copper-smelting in reverberatory furnaces thus described is the one usual in England. It is suitable to a variety or mixture of ores, without regard also to their associations in the way of siliceous matters, &c. But it entails a large consumption of fuel. For in the production of a ton of copper full 16 tons of coal will be expended. Hence, it is not so suitable to countries where fuel is scarce or dear.

Many patents have been taken out for improvements, mostly with a view to shortening the operations, and some, however, for wet methods, whereby poor ores may be advantageously reduced.

As one of the best of the former class of processes that of Napier may be given. He calcines a quantity of poor ore and afterwards mixes it with some rich ores containing a large percentage of copper. These are next roasted together, as in the second of the Swansea operations. When melted, and the scoriæ taken off, a quantity of salt cake (sodic sulphate) mixed with charcoal is thrown over and well mixed with the ores; or, in place of this, the rough sodic carbonate, known as soda ash, may be employed. The alkaline salt becomes a sulphide, and this is capable of combining with any arsenic, antimony, or tin, present in the ore. When this decomposition is complete, the matt is run out of the furnace into moulds so as to cast it into cakes, which, when removable, are put into vessels of water.

Solution takes place of the compounds formed with the soda salt, and a residue of ore is left in a powdery state, which is dried and calcined, by which the sulphur is readily expelled, and the copper oxidized. This latter is then mixed with ores containing no sulphur or arsenic, and some small coal or charcoal added for reduction of the metal. The whole is then heated in a reducing furnace, by which the pure metal is separated, and subsides under a slag which is left quite free from it.

In Birkmyres' process the sulphur in the copper pyrites is oxidized by sodic nitrate, and retained as sulphuric acid, and as sodic and ferric sulphates, the arsenic being expelled during roasting as arsenious anhydride, or acid. In working it the copper ore or sulphides are powdered, mixed with the sodic nitrate, and then roasted with exposure to the air; thus the sulphides are converted into sulphates, and these, with the sodic sulphate also, are dissolved out of the resulting mass in a tank of water, and the gangue allowed to subside; lastly, from the clear metallic solution the copper is precipitated by means of metallic iron.

In a process by Henderson very poor pyrites is also economically worked, from the capability of utilizing its sulphur for the manufacture of sulphuric acid. After the bulk of the sulphur has been roasted off, the residue of ferric oxide with a very small amount of copper, and also some sulphur and metallic impurities is ground, and mixed with a quantity of sodic chloride, and then roasted at a low red heat for some hours. Volatile chlorides, such as those of iron, arsenic, and antimony, are evolved, together with a quantity of hydrochloric acid, and of chlorine. Any copper is converted into cupric chloride, and the soda into sodic sulphate. The two latter are dissolved out by treatment with water, next with some dilute hydrochloric acid. The residue is then washed with water, and into these liquors bars of iron are put, which reduce the whole of the copper. This is further refined by poling. By this means of precipitation the water of copper-mines may have the copper reduced out of it. The copper results in this water from the oxidation of sulphides producing cupric sulphate, which is soluble.

Ores containing sulphides of copper in very small proportion to the ferric sulphide are in some places submitted to a concentrating operation, for which purpose they are roasted either in a heap or in kilns, in such a manner as that the copper by some means condenses itself into a mass forming a core or kernel, rich in copper within an outer shell of iron oxide, and sulphide, from which all the copper is found to be removed. The plan is termed ‘kernel roasting.’

The roasting operation is started upon fragments of the ore, by means of wood fires, but when once lighted, the sulphur of the ore itself burns and acts as so much fuel. The roasting occupies five or six months, after which the nodules are broken by hand, and the kernels separated from the surrounding material.

In the Venetian Alps, where this process is employed (at Agordo), the crust is utilized for the production of sulphuric acid from its sulphur.

Plattner, in his Röstprocesse, in explanation of the action going on, states that the pieces of ore are heated until some sulphur is volatilized, when it forms sulphurous acid, with atmospheric air, peroxide of iron being at the same time left. Some sulphurous acid escapes, but some takes more oxygen and becomes sulphuric, magnetic oxide and sulphate of iron being formed at the same time, continued reaction of the sulphuric acid converts these again into oxide of iron. The sulphide of copper is less oxidizable, and is also protected by a surrounding atmosphere of sulphur vapour; it fuses and combines with adjacent sulphide. The crust formed is porous, and allows the action to go on, but the crust of peroxide of iron becomes by degrees thicker; at the same time the copper sulphides become more and more concentrated, and form an actual core.

Percy* gives a very careful detailed account of this operation, but expresses himself as not satisfied with any of the explanations which have been given of the action taking place.

On the Continent, copper ores are generally reduced by means of the cupola or small blast-furnace, the fourneau a manche already spoken of; by it, very poor, and also very rich ores may be equally well worked, while the consumption of fuel (generally charcoal) is very small.

It will be evident that by such means rich ores, such as oxides or carbonates, may be at once reduced by simply heating in conjunction with some carbonaceous matter with some siliceous scoriæ added. But if sulphides are so treated, they require one or more previous roastings, analogous to those employed in the Swansea operations, and by which some sulphur, and the volatile bodies are driven off; but more especially for the purpose of oxidizing and separating the iron; after which they can be readily reduced in the blast-furnace.

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* *Metallurgy*, vol. i. page 439.

The blast-furnace operations, as carried out at Mansfeld, in Saxony, may be given as an example of working poor ore by this method. These are argillaceous schists containing a varying proportion of copper, ranging from 2 to 4 per cent only, but associated with a considerable quantity of bituminous matters, which assist in the reduction. The copper pyrites is diffused in the material in the form of small crystals.

About 100 tons or more are heaped in layers with wood, and inflamed, this roasting being carried on for four to five mouths. The ore in the end is thus rendered yellowish from the oxidation of the iron, and it is also made very friable. It is now mixed with some rich slags containing cupric oxide, a quantity of fluor-spar and some cupreous schists containing calcic carbonate; these two latter act as fluxes, while the slags afford material to convert the iron into silicate. This is introduced into a small blast-furnace, fig. 79. The average height is 16 feet; breadth at the tuyeres (*b*) 2 feet 2 inches, and at the widest part (*a*) 3 feet 6 inches. It is surmounted by a chimney of 40 to 50 feet in height. The tuyeres for carrying in the blast enter at (*b*) about 24 inches up the body sometimes at the back, at others on the opposite sides.

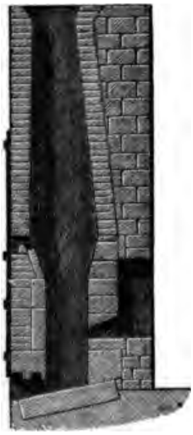

Fig. 79.

Calcined ore, mixed as above, is charged in, in alternate layers with the fuel, a mixture of charcoal and coke. The charge works off in about 15 hours. Two tap-holes are opened at the lower part of the crucible alternately; each communicates with a large receiving basin (*d d*), fig. 80. As soon as one has been filled the outlet (*c*) to the second is opened, and the melted materials separate into two layers, an upper one of slag, and a lower matt of copper, containing about 30 to 40 per cent of metal. Should the matt contain less than 30 per cent, the above operations are repeated so as to remove more iron sulphide, and so concentrate the copper before final reduction. Supposing, however, that the matt is sufficiently rich, it is next roasted five or six times in succession, in a series of square brick roasting-stalls (Röststadelen). These are formed of a back wall containing a flue for each stall; the six stalls are formed upon this wall by a series of short cross separating walls. They are closed in front after the charge is in by a temporary wall built up for each operation. In one of these a wood fire is got up, and the matt placed on this is roasted, after which it is removed and washed in water in a series of wooden vats so as to remove any cupric sulphate, which is always formed. These operations are repeated in the second stall, and so on throughout the whole, and occupy about seven weeks, after which the matts are ready for smelting into black copper in a second blast-furnace. This is a cupola resembling the first, but on a smaller scale. The product of the roasting stalls called 'Gahrröst' is charged in, mixed with a proper quantity of rich copper slags (usually about a $\frac{1}{6}$th of the weight of the roasted ore), and also with a quantity of charcoal or coke for firing. These slags afford siliceous matters to combine with iron oxide. After a period of about 24 hours, the operation being complete, the product is run into the receiving pots, where the black copper so called from its surface being covered with black oxide, subsides to the bottom; above this will be a matt of copper sulphide, and above all a layer of slag.

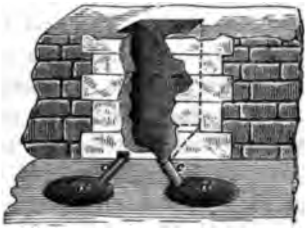

Fig. 80.

The black copper contains about 95 per cent copper, and it retains about 3 per cent iron with small quantities of silver, antimony, and sulphur.

The silver varies much in amount, and it is extracted by one of two processes. The first by liquation, after mixing the black copper with lead, has been already described under silver (page 155). The other is by amalgamation, and for this the gahrröst or matt produced from the roasting-stalls is first powdered, then moistened and roasted in a reverberatory furnace for about three hours. It is next removed and well mixed with about 10 per cent of salt, and an equal proportion of chalk; this latter is employed for the decomposition of the copper and iron sulphides which, existing in so great quantity as such in the matt, would occasion much loss of mercury, and hinder amalgamation. This mixture is dried, powdered, and again roasted for two hours.

The whole is then transferred to the Friburg barrels (page 164) and amalgamated in the usual way.

After separation of the amalgam, the cupreous residue is made into discs with clay, and smelted with siliceous material, whence black copper is obtained as before.

The refining of this product is commenced in a reverberatory, having an elliptical bed, *a*, of about 8 feet long by 6½ broad (fig. 81). This bed is formed of clay and coal-dust mixed and beaten well upon a foundation formed in several layers of clay, brick, and other material. At the back are placed two separate receiving basins, *b b*, of about 3 feet diameter each. The grate in front, *c*, is large for a wood fire, and at an angle at one side of this, enter the tuyeres, *d d*, of a blowing apparatus, by which a draught of air is directed upon the bed. The charge worked is 3 tons, worked

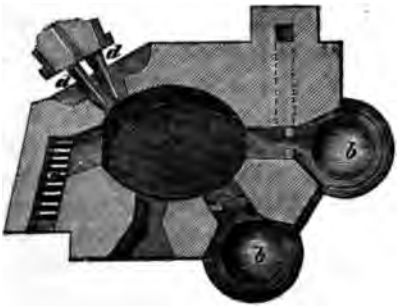

Fig. 81.

with a small amount of cement copper. When fused the tuyeres are directed upon the bath, a slag is thus formed upon its surface, and is removed as often as formed. The heat is raised, and the metal boiled for three-quarters of an hour. After this, assays are made as to the quality of the metal in the usual way, and if it is judged to be complete the charge is run into the basins. A little water thrown upon its surface causes discs or rosettes to separate, which are removed as they form, and plunged into water, thus further oxidation is prevented, and their red colour retained. This latter depends upon their containing suboxide, and hence also they need a second refining to render them malleable. This is done in another small furnace (fig. 82) composed of a hemispherical basin, *a*, of about 1 foot 4 inches in diameter, set in brickwork, and lined with a brasquing of 2 parts of powdered charcoal and 1 of fireclay. Into the back of it is carried a blast pipe, *b*. It is charged with ignited charcoal, on which the copper to be refined is laid, it is then covered with charcoal, and a moderate blast turned on. The charcoal and metal are then supplied until the basin is nearly full, the scoriæ flowing off into a receptacle. The assayer examines the metal from time to time, and when the refining is complete the blast is stopped, a little water thrown over the surface, the charcoal withdrawn and the scoriæ raked off, and on to the clean surface of metal' a little water is again thrown to set it. The rosette thus formed is removed, and this is repeated until all the charge is so removed. A 3½ cwt. charge is thus refined in about two hours, the malleability is not, however, quite perfect for manufacturing purposes, but requires for these, a second and more careful operation in the same hearth, after which it is cast in ingots.

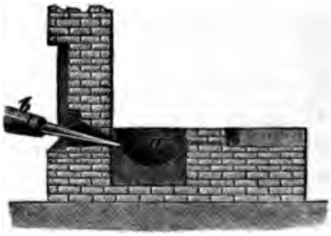

Fig. 82.

In Sweden and Norway copper is also smelted in blast furnaces, and at Atvidaberg in Sweden, the operations and the furnaces, &c., employed, are much the same as those just described as used at Mansfeld. The ore is first roasted in kilns or heaps, after which, mixed with slags in certain proportions, it is smelted in the first or ore furnace, which here is about 25 feet high by 13 feet external diameter. The regulus obtained after about 48 to 72 hours is removed, and roasted in a kiln several times till fit for the second or black copper furnace. For this the roasted regulus is mixed with certain slags and residues, and fused in the second furnace which differs from the first, in being of much smaller capacity. On tapping this furnace the product is cast in pigs and refined on the ore hearth until rendered tough and malleable. The ore hearth for this purpose being 2 to 2½ feet in diameter by 15 to 18 inches deep, and supplied with a blast tuyere at the back which turns down over the hearth when in operation.

Commercial copper is generally very nearly pure, yet it frequently contains traces of lead, silver, arsenic, bismuth, and at times tin, and traces of antimony. Some of these will materially injure the working qualities of the copper. Dr. Miller states that 10 ounces of antimony in a ton of copper will render it quite unfit to make brass which is required for rolling. Arsenic also is very injurious, especially if the copper is used for alloying purposes. A small proportion of tin will increase the tenacity of copper; if the quantity be large, it hardens it too much—in fact, produces bronze.

The purest form of commercial copper is that precipitated, as a crystalline powder, by means of iron from the sulphate found in solution in the water of some copper-mines. Such copper is called 'Cement copper.'

Commercial granulated copper is always tolerably pure, and on that account has generally been used for alloying metals for coinage. It is granulated by pouring the fused metal through a perforated ladle into a tank of water. If this water is previously heated the metal solidifies in compact rounded masses, known as bean shot copper. But if cold water is employed, the grains are flattened and flaky, and it is then called feathered shot.

The following methods will produce chemically pure copper :—

1st. Electrical precipitation by means of the battery. If the poles of a voltaic arrangement be immersed in a solution of cupric sulphate, the metal will be deposited in a solid state upon the negative pole, and, when washed and dried, is quite pure.

The cupric sulphate should for this purpose be purified by several re-crystallizations.

2d. By reduction of pure cupric oxide by hydrogen. For this purpose the oxide is placed in a bulb tube, to which apparatus is attached for evolving a current of dry hydrogen gas. The bulb is heated to somewhat below redness. The metal thus remains as a reddish brown powder.

3rd. Pure copper may be obtained in a pulverulent state by boiling a concentrated solution of cupric sulphate with distilled zinc. The copper solution must not contain any free acid. As soon as the blue colour of the salt disappears the zinc is taken out, the solution poured off the subsided copper, and the latter washed with some very dilute sulphuric acid. This is then poured off and the powder washed with hot distilled water. It is then pressed between folds of bibulous paper and carefully dried, and it is even better to dry it in a flask or retort through which a current of hydrogen gas is passed.

It may be obtained comparatively pure by igniting copper for half-an-hour in a covered Hessian crucible, having added one-third its weight of nitre. This addition oxidizes the traces of those metals with which it is contaminated.

Properties.—Copper is perfectly red in colour. It is sometimes found crystalline, either in cubes or octohedra, and it may be deposited in these forms by voltaic action if this be carried on very slowly. It is very ductile and tenacious, as well as malleable, but is hardened by rolling or hammering, and may be again softened by annealing. It becomes brittle when heated to near its fusing point. Pulverulent copper may be welded, by first pressing it into form, and then heating to a tolerably high temperature, but air must be excluded, for in fine division it is very oxidizable.

Copper fuses at 1996° F. = 1091 C., and is very little volatile; in those volatilized deposits where copper has been supposed to have been carried off, the sub-oxide will be mixed with it. It expands on solidifying, and absorbs oxygen: by some this is stated to be similar to the absorption of that gas by silver, but I believe it is a surface oxidation only. Copper is unacted upon by the air at ordinary temperatures, notwithstanding the moisture which may be present in it. It is readily soluble in nitric acid with evolution of nitrous fumes. By sulphuric acid it is only acted upon by the assistance of heat. Sulphurous anhydride is evolved and cupric sulphate formed. Hydrochloric acid acts slowly upon it, but if air be excluded it is inactive. Odling states that finely divided copper if boiled in hydrochloric acid will be dissolved with evolution of hydrogen.

Ammonia in like manner dissolves it if air assists, but potassa or soda is inactive upon it.

The specific gravity is about 8·93, varying slightly according to its state. It has a peculiar and disagreeable odour when heated, and a corresponding taste. The odour is communicated to the hands if they are moist when it is handled. Symbol, Cu''. Atomic weight, 63·5.

Compounds.—There are two compounds of copper with oxygen, viz., a suboxide or cupreous oxide, and a protoxide or cupric oxide, and there are corresponding chlorides and sulphides.

Cupreous oxide is formed if we heat metallic copper in the air, and break off the scale formed, but it is apt to be mixed with some protoxide if a current of air passes over it in forming it. It is found in nature in glassy masses of a deep red colour, and often in beautiful ruby octohedral crystals. It may be formed by heating the protoxide with finely divided copper (as filings) in the proportion of five parts of the former with four of the latter; in this way, when decomposition has taken place, by raising the heat to redness we get a fused mass. But in the laboratory it is commonly obtained in a red crystalline powder, consisting of octohedral crystals, by boiling equal parts of dibasic cupric acetate with sugar, and in four parts of water for about two hours. Regnault advises adding to a cupric salt some sugar and potassa, until the oxide which precipitates at first is redissolved, then on boiling the liquor the crystalline cupreous oxide is deposited.

Suboxide of copper forms subsalts, but these are not very stable, being readily converted into salts of the protoxide by absorption of oxygen. The chief use of this oxide is as a stain in glass-working. From it are produced, when pure, a most beautiful carmine red, as also several other tints, ranging from orange to deep red, these last are obtained by mixing with it a proper proportion of ferric oxide.

The brilliant reds of some early specimens of stained glass were due to this oxide, but in employing it much care and judgment are required, because from its unstable nature it is very liable to become protoxidized in the fire. And, again, its power is so intense, that unless the quantity employed be very small it will render the glass almost opaque. Composition, Cu_2 O. Atomic weight, 143.

Cupric oxide or protoxide may be formed by heating a sheet of copper in a good current of air. Cupreous oxide is first formed which passes to cupric oxide, if then the sheet is plunged in water it scales off, but mixed with some suboxide. It is obtained in a state of purity by dissolving pure electrotype copper in nitric acid, and evaporating to dryness. The resulting salt is then slowly heated to redness in a clay crucible, the acid is thus separated and decomposed, and the oxide left. It may also be obtained as a hydrate, by decomposing a pure copper salt, by means of potash, a bulky blue precipitate falls; this may be rendered anhydrous by boiling in water after it has been well washed. This oxide is soluble in acids, producing blue (and occasionally green) salts. It is soluble in ammonia, and hence this alkali, in place of permanently precipitating it from its solutions, colours them an intense blue; from this solution hydrated crystals will deposit, composed of cupric oxide combined with ammonia and water. If the cupric oxide be employed in enamelling or glass-staining, a green glass will be produced. Composition, $Cu\,O$. Atomic weight, 79·5.

Cupreous chloride may be formed by digesting copper in a solution of cupric chloride, or quicker by boiling finely-divided copper in the same. The blue colour of the liquid passes to brown, and at the same time white crystals of cupreous chloride are deposited. It may be obtained also by dissolving four parts of copper filings with five of cupric oxide in hydrochloric acid, or again by boiling cupric chloride with sugar.

It is insoluble in water, but soluble in strong hydrochloric acid. It has the property of reducing metallic silver and gold from their solutions. Composition, $Cu_2\,Cl_2$. Atomic weight, 198.

Cupric chloride is got by dissolving cupric oxide in hydrochloric acid, or metallic copper in aqua regia. It forms a very soluble salt, crystallizable in green needles, and very deliquescent. Composition, $Cu\,Cl_2$. Atomic weight, 134·5.

Cupreous sulphide, or subsulphide, may be formed by heating together the proper proportions of sulphur and copper. It is the produce also of the fourth operation in ordinary copper-smelting known as 'fine metal.' Composition, $Cu_2\,S$. Atomic weight, 159.

Cupric sulphide, or protosulphide, is the precipitate obtained in ordinary solutions of copper, by the addition of dihydric sulphide. Thus formed, it is a dark brown hydrate, soluble in nitric acid, and converted even by exposure to air into cupric sulphate. It may likewise be formed by heating together sulphur and copper filings in proper proportion. It is also precipitated by ammonio-hydric sulphide or potassic sulphide, but in the former salt it is slightly soluble. Composition, $Cu\,S$. Atomic weight, 95·5.

Alloys.—With mercury copper amalgamates, but the amalgam must be formed with a little management, for the metals do not readily combine. The best method of obtaining an amalgam is by just wetting a quantity of the pulverulent copper described at page 375, with a little mercurous nitrate solution. Thus the copper becomes well coated with mercury; this done, the mercury is poured upon it, and it may be to the extent of two or three times the weight of the copper, then by rubbing the metals in a mortar union of the two will be effected; and, lastly, perfect mixture is completed by gently warming in a crucible.

Copper may be mixed with silver in all proportions, and the chief use of this alloy is for the formation of coin and plate. Silver is much hardened by mixture with copper, and in small amount copper does not much colour silver; where, however, the quantity is considerable, the colour of the alloy becomes perceptibly yellow, and in equal parts will resemble brass in colour, while it is also rendered very hard. In England the proportions used for coin and plate are 11 oz. 2 dwts. of fine silver to 18 dwts. of copper, or decimally Ag 925 + Cu 75. This is a well-wearing alloy, but finer even than this is used for the striking of medals. Again, the Indian rupees are composed of 947 silver to 53 of copper. Of Continental coins the bulk are decimally alloyed. Thus French five-franc pieces, and French silver coin generally, are composed of silver 900 to copper 100; but some of the silver coin of Germany and Prussia is very coarse. From examinations of some of these made by the author, he finds that Prussian thalers average 811 Ag + 189 Cu; the German 24-kreutzer pieces, 586 Ag + 414 Cu; and the Prussian pieces of 5 silver groschen contain only 283 Ag to 717 Cu on the average. Hence the latter after a little wear have all the appearance of copper.

In silver bars alloyed with copper there is a great tendency in the copper to separate to some extent as the bar solidifies, and to pass off towards its edges, so that coins such as Mexican dollars, crown-pieces, &c., punched out of such a bar will always be poorer at the parts of their circumference corresponding to the sides of the bar, their quality increasing in silver towards their centre. I have carefully examined both Mexican dollars and crown-pieces for this, and found that the variation in such between centre and sides will range in the former one to six, and in the latter from one to four milliemes. The average of a number of experiments on crowns (viz. of twenty-four) gave a mean variation of two milliemes, and the quality in which greatest range is shown seems to be that of 900 silver to 100 copper.

Alloys of gold with copper have already been alluded to (page 269). Copper hardens gold very much, and when the copper is in any considerable quantity the gold is apt to be rendered more or less brittle by it, especially if the former metal be not thoroughly pure; hence great care is requisite in selecting copper for this purpose. At our Mint the kind known as shot copper is employed, as being a pure kind. In our own coin 916·6 parts of fine gold are alloyed with 83·3 of alloy, the whole of which may be copper. In France, Holland, and America, the same decimal system is pursued as with the silver coin; viz., 900 parts of gold are combined with 100 alloy; and in coin in which this alloy is all copper the metal, although rendered very hard, is nevertheless not at all brittle, if the alloying has been carefully done.

Copper and platinum in equal proportions form an alloy much resembling gold in colour. The specific gravity is also the same, but the metals require the strongest white heat for their combination.

Copper alloys with palladium, but the heat required for their union is also very great. Equal parts of the two metals form a light brass-coloured alloy, rather brittle, but Mr. Cock formed a ductile white alloy of four parts of copper to one of palladium. Copper and lead form a brittle alloy; indeed, when the proportion of lead is only a thousandth that of the quantity of copper, the latter is rendered very unworkable. If the quantity of lead be a hundredth of that of the copper, Karsten states that the latter will be quite useless. But copper will retain only a small portion of lead as alloy with it. Copper may be alloyed with bismuth, but the copper is thus rendered harder and brittle in working. Karsten states that even 0·6 per cent of bismuth will cause the alloy to crack at the edges when hammered. One part of copper with four of bismuth has a thorough red colour and the scaly texture of bismuth. Copper alloyed with zinc in various proportions forms the different kinds of brass. With tin it yields a variety of compounds, of which bronze is the chief. Lastly, with zinc and nickel, it forms German silver. These alloys will be examined in their appropriate places.

Discrimination of Copper.—1. Dihydric sulphide, or ammonio-hydric sulphide, throws down from either acid, alkaline or neutral solutions, a brownish black precipitate of cupric sulphide; not soluble in dilute acids or alkalis; soluble in potassic cyanide, and slightly so in ammonio-hydric sulphide, hence it is better precipitated by the first reagent.

2. Potash or soda precipitates a light blue basic salt, and on addition of excess this becomes a hydrated oxide, which on boiling is rendered brownish black and anhydrous; and the effect of fixed alkaline carbonates is ultimately the same, although at the first precipitation of the copper, it falls as a hydrated carbonate, the water and carbonic acid being subsequently driven off by boiling.

3. Ammonia, or its carbonate, gives a blue precipitate, which is immediately dissolved in excess, producing a deep blue solution. This same coloration is produced by ammonia in nickel salts. But distinction is made between them by the action of dihydric ickel sulphide, which in ~~metal~~ gives no precipitate if the solution be acidulated by sulphuric acid; and again by the difference of the precipitates produced by potassic ferrocyanide.

4. Potassic ferrocyanide gives a very characteristic brown precipitate, soluble in ammonia. If the latter be evaporated from such a solution, the cupric ferrocyanide is left unchanged. This precipitate is insoluble in hydrochloric acid. It is decomposed by potassa.

5. If a bar of iron be placed in a solution containing copper, the latter will be precipitated upon the bar in a metallic state; zinc or tin employed in the same way throws the metal down as a black powder.

Copper may be detected in exceedingly dilute solutions by placing a drop on a slip of clean platinum foil, if then a point of zinc be placed in it touching the foil a spot of reduced copper will be seen if present. When a copper salt is heated in the blowpipe oxidizing flame it will communicate a green tint to it; and if it be heated in a platinum loop with borax, a green bead is formed which will be blue when cold. In the reducing flame the bead will be reddish when cold, and if heated here upon a piece of charcoal, and with a little sodic carbonate as a flux, we get a bead of metallic copper.

Estimation of Copper.—Several methods have already been given under the head of Copper Assaying (page 353). And in the laboratory it may also be determined by precipitation as oxide, as sulphide, or as metallic copper. If the solution under examination contain only copper, or at any rate no other metal whose oxide is thrown down by potassa, we have only to add an excess of caustic potassa, and well boil the precipitate, and then wash, dry, and weigh. The precipitate contains 79·85 per cent of metallic copper. To ensure accuracy the solution must be dilute, and the precipitate very well washed to get rid of all the alkali, and it should be weighed directly it is cool.

When precipitated as sulphide the solution should be nearly neutral, and excess of dihydric sulphide added. The sulphide should be filtered and washed quickly. And it is usual then to oxidize by nitric acid, and again precipitate by potassa, and after this to proceed as before so as to weigh it as oxide.

To estimate as metal the solution is better if free from nitric acid. Place in it a piece of zinc, and add a little hydrochloric acid. Action commences immediately, and is carried on until the solution is colourless, and all the zinc completely dissolved. Any doubt as to all the copper being down may be settled by a drop of dihydric sulphide solution, supposing no other metal present precipitable by it. The pulverulent copper has the solution then poured off it, and is well washed and dried in a water bath, and weighed. If the operation is done in a platinum dish, it will be more speedy and effective being assisted by the galvanic action set up between the zinc and platinum. In analysing a mixture of mercury and copper, the amalgam is dissolved in nitro-hydrochloric acid, and having nearly neutralised the excess of acid by potassa, we add a quantity of potassic formiate, and digest at about 130° F. = 54°·5 C. Thus the mercury will be precipitated as subchloride; this may be collected on a filter, washed, dried, and weighed. Then the copper is to be separated and estimated as above.

The analysis of a mixture of gold, silver, and copper, has been already given at page 272.

CHAPTER XIV.

ANTIMONY.

The chief ore of antimony is grey antimony ore, a sesquisulphide, and this is the source of very nearly the whole of the antimony of commerce; ordinary grey ore contains also copper and iron. When nickel is present it is termed nickeliferous grey antimony. Small quantities of antimony are found native, in which case it is associated with silver and iron. Besides these, its sulphide is found in combination with that of silver, as in the ruby silvers; also with lead and copper; and in various other associations with lead, iron, copper, bismuth, or arsenic.

Antimony is found in Hungary and Bohemia, also in France. In various parts of Great Britain, in America, and in Borneo. Red antimony is a compound of sulphide and oxide of antimony, and the oxide itself is also found alone.

As the sulphide is contained in a matrix consisting of quartz, limestone, and heavy spar (or baric sulphate), the first operation preparatory to obtaining the metal consists in separating the sulphide from this gangue, which requires some care, as the antimonial sulphide is very fusible as also very volatile, and consequently much loss will arise if the heat employed be not carefully regulated. In Germany and some of the French works (and these countries supply the bulk of the antimony), the operation is effected in simple reverberatory furnaces, wherein the bed is made concave, and from its lowest point a channel is formed to convey the fused sulphide into proper receptacles; but as in these the above loss may be large without much care, the plan used at the

French mines at Malbose may be given as by far the best and economical method.

At these mines the operation is performed in a reverberatory furnace, but constructed with a dome-shaped arch, that is, arched each way; underneath this is placed a set of four fire-clay cylinders or retorts, A, which rise perpendicularly through rather larger openings in the arch; these openings being covered by fire-clay covers. The cylinders stand perpendicularly upon the strong cover of an oblong chamber formed below on each side, wherein a crucible, B, is placed immediately below each cylinder for the purpose of receiving the liquid sulphide; which passes from the clay cylinder down into the crucible by a hole in the chamber cover. The grates run from back to front, and are placed on each side of the crucible chambers at about the level of the pots, the heat being allowed to pass into them by flues.

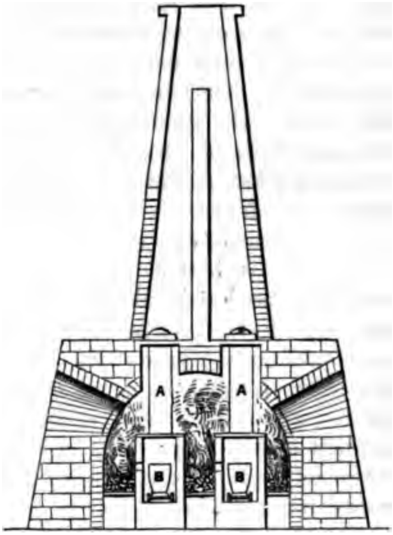

Fig. 83.

In working, the crude ore is put into the clay cylinders, and wood fires are kindled upon the grates, the draught of which is kept up by a chimney which rises over each pair of cylinders. As the sulphide fuses out of the ore it passes down, and is received in the crucible below; the latter, being of cast-iron, is lined with clay, in order to get the cake of sulphide out more easily when cold. The operation upon a charge of ore occupies about three hours. The weight of a charge is 5 cwt., and the ore yields on an average half its own weight of sulphide, requiring about 25 lbs. of coal per hundredweight for working. The clay cylinders last about three weeks each.

The product so obtained is commercial crude antimony, which is really a sulphide. From this the metal is obtained by first powdering it, and then heating upon a reverberatory bed, a roasting or dull red heat being employed. By this much of the sulphur is driven off, together with any arsenic which may have been present; some antimony oxide is generally lost, also, during this roasting. The two former escape as sulphurous and arsenious anhydrides. The residue, which consists of a mixture of teroxide and tersulphide of antimony, is now worked up with one-fifth its weight of charcoal, which has been previously saturated with a strong solution of sodic carbonate, or one part of coal with half its weight of potassic carbonate may be used. This mixture, placed in crucibles, is heated in a wind-furnace to redness; thus the metal is reduced and sinks to the bottom of the pots, under a slag composed of sulphides of sodium and antimony. This latter is separated from the pure metal and sold as 'crocus of antimony.' The yield of metal, owing to this and other loss during its extraction, always falls short of the true contents of the ore. It averages about 60 per cent of the whole. The metal itself is known as 'regulus of antimony,' and is now cast into ingots, in greased iron moulds.

The ore is sometimes smelted so as to yield the metal at one operation, especially if it be rich. At Linz they roast the crude ore for about eight hours, mixed with an alkaline carbonate and a quantity of iron; employing a reverberatory with a bed formed of clay and sand. Thus a very impure metal is separated, which requires purification.

At the Rotherhithe works, until lately, they were in the habit of reducing ores of about 55 per cent in this way, but using crucibles for the purpose of the fusion. The ore was charged into the pots in pieces of about two inches in diameter. Then the alkali, and lastly some pieces of scrap iron. Upon heating, the mass fuses, and the iron is then well mixed with it. It takes the sulphur forming a sulphide of iron, and the antimony is set free, On pouring the contents of the crucible into an iron mould the antimony separates from the iron sulphide.

It may be refined by mixing it in powder with half its weight of antimonious oxide and fusing; thus iron and copper (if present) are oxidized, and arsenic is also separated; or the impure metal may be fused with nitre, which will oxidize its impurities. They have, however, discontinued the process as unremunerative.

Chemically pure antimony is best obtained by Wohler's method, which is as follows:—Four parts of metallic antimony are powdered with two of dried sodic carbonate, ~~soda~~, and five of sodic nitrate. This mixture is heated to redness, when oxidation of the antimony and arsenic (if the latter be present) takes place at the expense of the oxygen of the sodic nitrate, and sodic antimoniate and arseniate are formed. When deflagration ceases, the pasty mass is kept over the heat for about half an hour, the operator now and then squeezing it with an iron spatula; after which it is removed, and when cold, powdered and thrown into boiling water; this dissolves away the arseniate, while the insoluble antimoniate is left; this is well washed with hot water. It is then removed, dried, and fused with half its weight of crude tartar. The product of this fusion is next broken up and thrown into water; a copious evolution of hydrogen is at once set up from the oxidation of the potassium, for the mass so treated is an alloy of antimony and potassium. The residue of this action is a powder composed of antimony, with any iron and lead which may have been contained in the original metal. To remove these, about one-third of the powder is treated with nitric acid, so as to oxidize it; this portion, when washed and dried, is mixed with the residue of the metallic powder, and the two fused together in a covered crucible, by which the pure antimony is separated and subsides under a slag composed of the foreign oxides.

Properties.—Antimony is a bluish-white metal, which, from its crystalline nature, readily breaks up, showing beautiful clean facets. The surface of a fused mass of the metal is commonly, when cooled, covered with stellate crystals, formed according to Rammelsberg by a number of rhombohedrons, gradually decreasing in size. These are placed in three parallel rows, forming three radiated groups from one centre joined at their edges.

By slow cooling it may be obtained in distinct rhombohedrons. This crystalline condition is much due to a small amount of impurity, and, indeed, may be increased by addition of other metals — small quantities of tin, for example — and, on the other hand, Matthiesen has shown that pure antimony is not easily crystallized.

It fuses at 1150° F. (= 621° C.), and volatilizes at a white heat. If exposed to air during fusion, it is speedily oxidized; but at ordinary temperatures it is not acted upon by the air. It is soluble in hydrochloric acid aided by heat, hydrogen being evolved; but by nitric or sulphuric acid it is oxidized. In the former case a white insoluble oxide results, and in the latter a sulphate also insoluble, sulphurous anhydride being evolved. Aqua regia dissolves it readily. Miller states that 'metallic antimony when in fine powder is readily dissolved by digestion with a solution of one of the higher sulphides of potassium, whilst the lead, iron, copper, bismuth, or silver, which it may contain, is left undissolved. Small quantities of arsenicum, or tin, if present, enter into solution with the antimony.' The specific gravity of antimony is 6·714; its symbol, Sb'''; atomic weight, 122.

Combinations.—With oxygen antimony forms three compounds: the first, or antimonious oxide, has basic properties, and is the base of all salts of antimony; the second is antimonic acid (or anhydride); and the third, a compound of these two has consequently been termed antimonious antimoniate.

Antimonious oxide (the old teroxide) is readily formed by oxidizing the metal by means of strong sulphuric acid and heat: thus, as has been before stated, on evaporating all the residual acid away, a white powder is left—the sulphate of the oxide in question: but to free this entirely from sulphuric acid, it is digested in a solution of an alkaline carbonate, washed and dried.

It may be formed in the dry way by burning antimony in a crucible wherein the air is free to enter: thus white fumes of oxide may be condensed in convenient vessels. There is also a scarce ore of antimony found native, called white antimony ore, which is antimonious oxide. Symbol, Sb_2O_3; atomic weight, 292.

If antimony is treated with nitric acid, it is oxidized, and, upon driving off the acid by a moderate heat, a pale yellow, insoluble powder will be left. This is the second named oxide, viz. antimonic acid, or anhydride, having the composition Sb_2O_5. If this is heated strongly, one-fifth of the oxygen will be driven off and the third compound left as a white powder, and of the composition Sb_2O_3, Sb_2O_5. It is, in fact, a salt wherein one oxide plays the part of acid, and the other of base.

There are two chlorides, the first or trichloride, or antimonious chloride, is the compound known as 'butter of antimony.' It may be obtained by digesting sulphide of antimony in strong hydrochloric acid, with the addition of about a fourth its weight of nitric. This is heated until the solution from a deep yellow becomes colourless. If it be evaporated, and the residue then removed and distilled, a white, semi-transparent crystalline solid is obtained, of about the consistence of butter. The retort used must be wide-necked, or the product will condense in it and so stop it up; or it may be obtained by adding two parts of sodic chloride to one of antimonious sulphate, mixing well and distilling. This solid body is very deliquescent, and fuses to a colourless oily liquid, which fumes in the air, and which, when thrown into water, is decomposed, an oxychloride being precipitated. Composition, $Sb\,Cl_3$. Antimonic chloride, or pentachloride of antimony, may be formed by passing dry chlorine over a quantity of powdered antimony, the latter being slightly heated. In this way the metal may be said to be dissolved by the gas, and a dense liquid is the result. When pure it is white; if it has a yellow tint, it contains chlorine in solution. This is very volatile, and evolves white dense fumes on exposure to the air. Composition, $Sb\,Cl_5$.

Antimony forms two sulphides corresponding to the two first oxides, viz. antimonious and antimonic sulphides. The first, or antimonious sulphide, is the one contained in the ordinary ore of antimony. It may also be prepared in the wet way, by digesting Kermes' mineral with tartaric acid. This is a compound of antimonious sulphide and oxide, the latter being combined with a portion of potassa. On heating this in tartaric acid, the antimonious oxide and the potassa are both dissolved out, and pure tersulphide is left. Or, if antimonious oxide be melted with sulphur, a portion takes the oxygen of the oxide and forms sulphurous anhydride, while another portion combines with the antimony to form antimonious sulphide, which is left as a crystalline mass on cooling. $2\ Sb_2\ O_3 + 9\ S = 2\ Sb_2\ S_3 + 3\ S\ O_2$. Composition, $Sb_2\ S_3$.

Antimonic sulphide may be obtained by passing dihydric sulphide into an acid solution of antimonic chloride. It falls as an orange yellow powder. It combines as a sulphur acid with sulphides of the alkali metals as bases forming salts. Composition, $Sb_2\ O_5$.

Alloys.—The useful alloys of antimony are chiefly those it forms with lead and with tin, constituting the various forms of type-metal, Britannia-metal, some kinds of pewter, &c. These will be considered under Tin. The use of antimony in alloys is to harden them, and, moreover, it causes expansion in most alloys, and thence sharp casts, thus it is of great value to the type-founder. But in many cases it renders an alloy brittle, and it is when associated with the noble metals or with copper, peculiarly injurious to them as regards their malleability, ductility, &c. Hence such alloys are never made; indeed, it may be said to form brittle alloys with most of the malleable metals. In regard to gold, its admixture is particularly to be guarded against, for a single grain added to 200 of perfectly fine and malleable gold, will render it completely brittle in texture, even 1 in 2000 injures its malleability.

Tests for the Detection of Antimony.—1. Dihydric sulphide added to an acidulated solution of antimony occasions an immediate precipitate of very characteristic orange-red colour; but if the solution be alkaline, no precipitate will be produced, and but a partial one in a neutral solution; hence the sulphide so thrown down is soluble in excess of potassa. It is also soluble in ammonio-hydric sulphide.

2. Ammonio-hydric sulphide throws down the same, but the precipitate is soluble in excess of the precipitant. It may, when so re-dissolved, be thrown down again by an acid; but its colour is always lighter under these circumstances, from sulphur being precipitated with it.

3. Potash, or ammonia, or the carbonates of these, throw down a bulky white hydrate, but not if the solution contain tartaric acid. The precipitate when formed by potash is soluble in excess of alkali, but if by ammonia or alkaline carbonates, it is nearly insoluble.

4. If the solution be treated with sulphuric acid, and into this metallic zinc be put, the mixture evolves a gaseous compound of hydrogen and antimony (antimoniuretted hydrogen); and if the gas escaping from the jet of a gas-bottle be inflamed, and a plate of cool porcelain be momentarily held over this flame, a deposit of metal is formed as a dark leaden-looking spot, just at the point of contact of the flame.

Lastly, If a hydrochloric solution of antimony be treated with a quantity of water, an immediate precipitate of an oxychloride falls. This may be dissolved in tartaric acid, the addition of which latter to the water employed will prevent its precipitation. This solubility in tartaric acid distinguishes it from the analogous bismuth precipitation.

Estimation of Antimony.—This can only be done by its precipitation as sulphide, and subsequently separating the sulphur of the latter, after having previously got its weight. Then, by estimating the sulphur, the difference between its weight and that of the whole precipitate gives that of the antimony. We may operate thus:—To the hydrochloric solution add a little tartaric acid, and then pass in dihydric sulphide. Thus the sulphide is thrown down. And now all excess of the precipitant must be got rid of by driving it off at a temperature of about 100° F. Wash, dry, and weigh the sulphide, having noted the weight. Next dissolve it in aqua regia; then mix this with a solution of tartaric acid, and precipitate the sulphuric acid (formed by the oxidation of the sulphur of the sulphide) by means of chloride of barium. From the weight of this when washed, dried, and ignited, that of the sulphur is got at; and the loss represents the antimony.

CHAPTER XV.

URANIUM, TITANIUM, AND CHROMIUM.

THREE metals may now be briefly examined, as some one or more of their compounds are employed in the arts, and in each case principally as colouring agents in glass and porcelain-working. For this purpose uranium affords an orange yellow and also a black; titanium, a light yellow; and chromium, a green; and by modification of treatment, a pink enamel may be obtained from the latter also. The first is one of the fourth division, and the second and third belong to the third division of metals.

URANIUM.

The metal itself is a white metal, resembling polished iron, somewhat malleable, and of very high specific gravity. The source of this, as of all preparations of uranium, is principally from a Bohemian mineral called pitchblende, a natural compound of two oxides of uranium, the protoxide and sesquioxide, uranous, and uranic oxides. The minerals uranite and chalcolite (containing this metal) are comparatively rare. From pitchblende uranic nitrate is first obtained, and from this salt all other compounds are prepared.

The mineral is first powdered very finely, after heating and quenching in water, then digested in dilute hydrochloric acid. This separates calcic carbonate, magnesia, and oxides of copper, and manganese. It is next washed, mixed with charcoal powder, and ignited strongly; this separates arsenic and some sulphur.

It is now digested in strong hydrochloric acid for the removal of lead, iron, and copper. After which a final roasting gets rid of the remaining sulphur, and as much arsenic as possible.

The mineral, so far purified, is now treated at once with nitric acid. The solution so obtained evaporated nearly to dryness, and the residue subsequently dissolved in water; part will remain undissolved, consisting of ferric arseniate, with some plumbic sulphate, the whole forming a red insoluble powder. The solution is filtered, in order to separate this; and dihydric sulphide is passed through the mother liquor after removal of the crystals. This will throw down a further portion of arsenic, as sulphide, together with cupric and plumbic sulphides. The liquor is then filtered, and again evaporated, and set aside for crystallization. Lastly, the whole produce of uranic nitrate is purified by recrystallization.

If it be desired to obtain the metal, it is done as follows:—A portion of nitrate is heated to decomposition. In this way the nitric acid is driven off, and an oxide left. This is mixed with some charcoal, and placed in a combustion tube, with an arrangement for evolution of dry chlorine attached. The tube is then heated and the gas passed into it. Thus it combines with the uranium, and the chloride produced rises in fumes, which condense into green deliquescent crystals in a cool part of the tube. This is uranous chloride, having the composition $U\,Cl_2$.

The next step consists in speedily making a mixture of this with half its weight of potassium; and the quantity operated upon should be somewhat less than 200 grains of mixture, as the reaction of the two is very violent. For this reason also the platinum crucible, in which the reduction is made, should have its lid fastened on, and be quite enclosed in a second and larger pot. A gentle heat is at first applied, and when the violence of the action is over, this is raised so as to volatilise the remaining potassium and also to fuse the potassic chloride formed, as well as to allow of the subsidence of the uranium in it. When cold, the excess of potassium and chloride is removed by solution in water, the metal being left. Its atomic weight is 120. Symbol, U.

There are two simple oxides of uranium, and by their combination with each other two other compound oxides are formed. The first is a protoxide, or uranous oxide; its composition is expressed by the symbols UO.

The second is the sesquioxide. This is the one employed for producing the orange-yellow porcelain colour. It is prepared commercially by precipitating uranic nitrate by means of ammonia: but it is not then true; for this oxide has a tendency to act as an acid in the presence of alkalis, and to combine with them and form salts: therefore, in this case it so combines with the ammonia, and a hydrated uranate of ammonia is produced. Moreover, the ammonia and water cannot be driven off by heat, so as to leave the oxide sought, for either the green or black oxide will be left, according to the degree of heat used. The only way to obtain a true sesquioxide consists in precipitating the purified nitrate by oxalic acid; thus an oxalate is obtained. This is then exposed to the sun's rays, when carbonic anhydride will be eliminated by the decomposition of the oxalic acid, and a purplish powder is left, which is the green oxide of uranium in a hydrated state. By exposing this to air, enough oxygen will be absorbed to convert the whole into sesquioxide, and from this last the water may be driven off by heating carefully to 570° Fahr. (= 300° C). The anhydrous sesquioxide thus produced is a dull red powder, of the composition U_2O_3. The operation, however, requires extreme care in all its stages.

The black oxide, which is employed for the black enamel of porcelain, is obtained by heating intensely uranic nitrate. Thus a black powder results, which has the composition $2\,UO + U_2O_3$.

The green oxide is obtained from the last by oxidizing it in the air, by means of gentle heating; but if, when prepared, the heat be raised strongly, it will be reconverted into the black oxide. Its composition is $UO + U_2O_3$.

Discrimination of Uranium.—1st. Dihydric sulphide gives no precipitate.

2nd. Ammonio-hydric sulphide gives a brownish-yellow sulphide; but if the uranium exist as protoxide, this will be black.

3rd. Potassic ferrocyanide gives a brown, just like the precipitate formed by that reagent in a copper solution; but it may be distinguished from the latter by a portion of the solution not being rendered blue on adding ammonia.

TITANIUM.

The mineral rutile, a nearly pure oxide, is the chief source of the various preparations of this metal. It is a compound of an atom of titanium with two of oxygen. In titaniferous iron, and in iserine, this same oxide is associated with that of iron. Titanic acid is present in many clays, and in them has been mistaken for silica. The metal itself is commonly described as a purplish-red powder; but it has been shown by Deville, Wohler, and others, that titanium has an extraordinary affinity for nitrogen, and that the red product of some of the methods employed for its preparation is really titanic nitride; as also are the hard, cubic, copper-coloured crystals, frequently found in iron furnaces, and which have hitherto been regarded as the metal itself. These latter contain, moreover, a certain quantity of titanic cyanide.

Deville obtains the metal in square prismatic crystals, by first forming titanic chloride; for which purpose he heats a mixture of titanic acid or anhydride and charcoal in a tube, and passes over this a stream of dry chlorine gas. Having thus obtained a volatile liquid (a bichloride), he passes its vapour over fused sodium, and thus gets the metal itself.

It is best obtained by decomposing the double fluoride of titanium and potassium, by means of hydrogen: thus formed, it is a pulverulent metal of a greyish tint. It is, however, very quickly oxidized, and converted into titanic anhydride by a slight rise of temperature, while exposed to air. Symbol, Ti. Atomic weight, 50.

Titanium forms three oxides, but it is only the highest (viz. titanic dioxide or anhydride, known as titanic acid) which is of importance, this being the one employed to obtain a pale yellow porcelain colour.

Rutile, being nearly pure titanic acid, is employed for its preparation; for which purpose it is powdered and mixed with three or four times its weight of potassic carbonate. These are put into a crucible and fused, and the mass so obtained subsequently digested in water. Every two proportionals of titanic acid will in this way have combined with one of potassa, and formed an insoluble salt, which is to be separated and treated with hydrochloric acid, and, when dissolved, an excess of caustic ammonia is to be added to the solution. Thus a mixture of titanic acid with oxide of iron, and perhaps tin and manganese, is thrown down, in which the three latter may be converted into sulphides on adding ammonio-hydric-sulphide, and that without action upon the titanium oxide, which remains as such. Next, a quantity of sulphurous acid in solution is poured upon the mixture, whereby the sulphides will be dissolved and the titanic acid left. It only remains to wash thoroughly, and dry it, and thus it is a pure white hydrate of titanic acid.

This compound is soluble in sulphuric and hydrochloric acids, but, if heated strongly, it assumes a yellow tint and becomes anhydrous. On cooling, it resumes its white colour, but will then be insoluble in most acids, or in alkaline solutions, except it be put into boiling sulphuric, or digested with hydrofluoric acid. Composition, $Ti\,O_2$. Atomic weight, 82.

Discrimination of Titanium.—The acid, from its appearance and chemical bearings, may be confounded with that of tin, or with silica. From the former it may be distinguished by heating it before the blowpipe. Tin, when heated in the reducing flame, would, on the addition of a little sodic carbonate, be at once reduced to a metallic bead; but titanic acid, if mixed with borax or microcosmic salt, and exposed to the same flame, would give a blue glass; if heated in the oxidizing flame, the glass formed is colourless. It may be distinguished from silica by fusion with hydro-potassic sulphate, by which it will be rendered soluble, so as to form a clear solution on boiling in water; silica being untouched by such treatment. 2d. If a solution of a titanate be tested by potassic ferro-cyanide, an orange-yellow precipitate is formed, which is very characteristic.

CHROMIUM.

This metal exists in an ore known as chrome iron ore, which is a mixture of sesquioxide of chromium with oxide of iron. From this the first preparation obtained is always potassic chromate or dichromate, and all other compounds are separated or converted from the latter. This is the result of the large application of the dichromate to calico-printing and dyeing, which causes its manufacture to be an important one. It is largely carried on at Glasgow, and the product sold under the name of chrome.

The metal is obtained by first forming a chromic chloride, and then decomposing it by potassium: thus it is obtained pure, as a dark-grey powder, readily oxidizable by heating it in the air. Fremy obtains it in a crystalline condition by heating chromic chloride to redness in a porcelain tube. The chloride is placed in a boat or tray, and the vapour of sodium is then passed over it, which reduces the metal. It may, however, be obtained nearly pure by heating a mixture of chromic oxide with one-fifth its weight of carbon. This is to be made into a paste with oil, and then heated for about two hours in a wind furnace: thus a porous mass of the metal is left, containing, however, a small quantity of combined carbon. Symbol, Cr. Atomic weight, 52·5.

It has been stated that the compounds of chromium are obtained from chrome iron ore, by first forming potassic dichromate. Now, as the ore is not attacked by acids at all easily, the first step in this preparation is powdering it; after which it is mixed with sufficient nitre to oxidize the chromium; a quantity of potassic carbonate being also used: these are exposed to a red heat in a reverberatory furnace, and during the heating constant raking is kept up, in order to expose the whole well to air, and so facilitate the changes to be produced. Thus the chromic oxide, by the oxygen of the nitre, becomes converted into chromic acid; this decomposes the potassic carbonate by combining with its alkali. The roasted materials are next digested in water; thus the new-formed salt is dissolved, and an insoluble residue left; but as the latter is not yet exhausted of the 'chrome,' it is set aside for a second treatment. The yellow solution is filtered or syphoned off, and just neutralised with nitric or sulphuric, or better, with acetic acid. Thus the salt, which originally was a neutral chromate, is converted into a dichromate, which being a far less soluble salt than the former, much contributes to its purification from adherent potassic nitrate. Hence also the preference to be given to acetic acid in its preparation, for with potassa this acid forms an exceedingly soluble salt, much more so than potassic nitrate, which results from using nitric acid; while potassic sulphate, which is formed where sulphuric is employed, is yet more insoluble, and, therefore, economy in the price of acid is the only reason for employing the latter. The potassic dichromate so obtained forms beautiful red four-sided tabular crystals, from which neutral chromate is best formed by dissolving them, adding a proportional of potassic carbonate, and recrystallizing.

Chromium forms four oxides. The two first, viz. the protoxide or chromous oxide, $Cr\ O$, and the sesquioxide or chromic oxide $Cr_2\ O_3$ have basic properties. The third is a compound one, formed of one proportional of $Cr\ O$ with one of $Cr_2\ O_3$. The fourth is chromic acid or anhydride $Cr\ O_3$. A fifth has been described as composed of $H\ Cr\ O_4$, but it is little known.

Of these, the one employed as a porcelain colour is the sesquioxide, in its anhydrous state, wherein it is but little acted upon by acids, and may be employed with most fluxes, and so heated strongly without change. It is this oxide which gives colour to the emerald, and also to some analogous minerals. It may be prepared by several methods, but of these the three following may be taken as most practical.

1st. Potassic dichromate is put into a crucible, and heated to a white heat. Thus it is converted into neutral chromate, and the atom of chromic acid taken away loses as much of its oxygen as leaves it in the state of sesquioxide of chromium. The fused mass is treated with water; by this the chromate is dissolved, and the oxide remains as a green powder.

2nd. Potassic chromate is added to a solution of mercurous nitrate; thus a precipitate is formed of mercurous chromate. This is washed, dried, and heated to redness. The whole of the mercury is thus volatilized, and with it a portion of the oxygen; the sesquioxide of chromium being left.

3rd. Potassic dichromate may be heated in a charcoal-lined crucible, or in an ordinary pot, if previously mixed with one-fourth its weight of starch, both being powdered together. This, by oxidation, produces carbonic anhydride, which converts the potassic dichromate into carbonate; the sesquioxide of chromium, resulting from the decomposed chromic acid, will be separable by washing away the alkaline carbonate.

Sesquioxide of chromium is a deep-green powder. In its anhydrous state it is little soluble in acids; but when hydrated, as when precipitated by the action of alcohol on potassic dichromate, it dissolves readily in acids, forming uncrystallizable salts. The anhydrous variety produces a deep-green enamel upon porcelain when used alone, but a beautiful rose-pink may be obtained also. In the pink colour, however, it is probable that the oxide is one of higher degree of oxidation.

The material for its production is thus prepared:—Four parts of potassic chromate are mixed with 34 parts of chalk and 100 of stannic oxide. These are heated to redness in a crucible, and the resulting mixture powdered, and then treated with weak hydrochloric acid until it assumes its proper tint, viz. a fine rose-pink. This is much used in earthenware painting.

Composition of sesquioxide of chromium, $Cr_2 O_3$. Atomic weight, 153.

In the discrimination of chromium the reactions vary according to the degree of oxidation of the metal; but the following tests are indicative of the sesquioxide in solution:—

1st. Dihydric sulphide gives no precipitate.

2d. Potassic sulphide throws down the green sesquioxide, setting free dihydric sulphide.

3d. Potash or soda precipitates a hydrated sesquioxide. The precipitate is soluble in excess of the former, but it will be re-precipitated again on boiling, or on addition of ammonic chloride.

4th. Ammonia throws down hydrated chromic oxide, varying as to appearance, dependent on concentration of the solution, method of precipitation, &c.

5th. If sesquioxide of chromium be fused with potassic nitrate, potassic chromate is formed; which latter, as all salts of chromic acid, may be distinguished by the yellow precipitate they give in salts of lead, and the red one in a solution of argentic nitrate.

6th. Before the blowpipe, if heated with microcosmic salt in either flame, a glass is produced, which is yellowish-green while hot, and emerald-green upon becoming cold.

CHAPTER XVI.

ARSENIC.

The metal arsenic, or arsenicum, may be obtained in the laboratory from its most common compound, viz. arsenious acid or anhydride (the white arsenic of the shops), by simply heating the latter with two parts of black flux, or with powdered charcoal. For this purpose an intimate mixture is made of them, and placed in a crucible; upon this a second one is luted, and just down to the lute-junction a perforated plate of iron is slipped over the upper one: this protects the latter from heat during the reduction of the metal. The lower pot is then well heated up, and the reduced arsenic, being volatile, sublimes, and is condensed in the upper, cooler pot.

But the metal is reduced, on the large scale, generally from some arsenical ore, and mispickel, or arsenical pyrites, is the one most in use. This, when pure, contains 42·88 per cent of arsenic. It is an arsenio-sulphide of iron (Fe As S). This is roughly powdered and heated in long retorts of from 4 to 5 feet in length, some pieces of iron being first mixed with it. A receiver being luted on, the retort is heated to a moderate temperature, when the arsenic sublimes off and condenses in the receivers. This product is less pure than that reduced from arsenious anhydride, and is purified by a second sublimation, but it is sufficiently so for its uses as an alloying metal. It is used for alloying lead in making shot; also in some forms of opal glass.

Thus it forms a steel-grey brittle cake, of crystalline texture;

but it soon loses its brilliancy, and, if exposed to damp air, it blackens, crumbles, and partly decomposes. It is easily powdered, is volatile at 360° F. = 182° C., and, like all the compounds of arsenic, evolves a peculiar odour of garlic. Its specific gravity is about 5·90; symbol, As'''; atomic weight, 75. In England much arsenic is obtained from ores of tin, the roasting of which evolves arsenious anhydride; but on the Continent arsenical cobalt and the arsenical pyrites mentioned are the chief sources.

The important compound of arsenic is the sesquioxide, or arsenious acid, or anhydride, and at many places the production of this is the first operation upon the ore. At the Silesian works arsenical pyrites is first roasted in a furnace constructed with a large muffle-like chamber, so placed, as that the flame and heat of a separate fire shall well circulate round it. About half a ton of the powdered ore is placed in the muffle at a time, being spread evenly over the floor. A dull red heat being got up, it is steadily maintained for about twelve hours, towards the latter part of which time it is allowed to fall somewhat. From the back of the muffle an opening passes into a large condensing room—a large chamber placed behind the furnace; from this any uncondensed matters pass to a second and third, and again from these into the first of a series, called at the Silesian works at Altenberg 'the poison-tower,' and composed of some three floors of double chambers. From the last and upper one a flue passes out into the air, and by this much sulphurous anhydride (which is uncondensable) passes away. The continual current passing through the apparatus serves to waft the arsenical vapours into the chambers; and they will be all condensed, the products in the first chambers being the purest, those condensed farthest from the muffle being generally contaminated with sulphide of arsenic, from combination with sulphur. The chambers are left from six weeks to two months between each emptying, and the dry pulverulent condition of the product makes the operation one of much danger to the operatives who are clad for the purpose in a close dress of leather and with their mouths and nostrils protected by a kind of respirator formed of wet cloths.

The first product is from its impurity submitted to sublimation. At Reichenstein, for this purpose, a series of deep iron or earthen pots are set in ordinary stove-holes, the latter working into a common shaft or flue. Upon the flange formed to each pot is built up a series of ring-connecting pieces, and on the top of these a funnel-shaped connector rises up and terminates in a large condensing chamber, formed well up above all.

The pots are charged with the crude acid, and then all joints well luted up. A gentle fire is then got up to each, and, after about half an hour, raised and maintained at a proper heat for subliming the acid. After about twelve hours a charge of about 3 cwt. will all have worked up into the cylinders above the pots, where it is found as a vitreous mass, if the heat has been well managed.

The upper portions, again, being less pure, are reserved for re-sublimation with a fresh charge of rough acid. The condensing chamber above serves to retain any which may rise if too great heat has been used, as also the sulphur products separated from the rough acid.

Arsenious anhydride, as thus prepared, is a clear, semi-transparent solid, lamellated, as might be expected, from its gradual deposit by sublimation. By exposure to air it soon loses its transparency and whiteness. Sublimation may be effected at about 380° F. (= 193° C.), and it may be condensed in small clear tetrahedra and octohedra. In commerce it is usually sold as a white powder, which, when examined by a lens, is found to consist of such minute crystals. It combines with bases as an acid, and in this way forms many valuable salts. Thus tripotassic arsenite, the essential ingredient of 'Fowler's solution,' forms a medicine much used internally. Cupric (or hydro-cupric) arsenite, known as 'Scheele's green,' constitutes a valuable pigment; and there is a somewhat similar pigment, composed of three proportionals of cupric arsenite combined with one of cupric acetate.

Arsenious anhydride is powerfully antiseptic, preventing decomposition in organic substances.

Arsenious anhydride dissolves in hot hydrochloric acid, and by treating it with nitric it is converted into an acid of higher grade, viz. the arsenic acid. The same change is produced by warming the hydrochloric solution, and adding potassic chlorate in small repeated quantities.

Arsenic acid is a compound of $As_2 O_5$, and forms a white mass, which is capable of crystallization; but both in this, as in its amorphous state, it is very deliquescent. It forms with bases an important class of salts called arseniates. The composition of arsenious anhydride or acid is $As_2 O_3$. Atomic weight, 198.

The bodies known as orpiment are sulphides of arsenic. The red variety, or realgar, is at times found native, in a crystalline state. It may be prepared artificially by heating 100 parts of arsenious acid with 57 of sulphur. It forms a scarlet amorphous substance, which, when powdered, gives an orange-yellow powder. It is composed of $As_2 S_2$.

Yellow orpiment is a sesqui-sulphide, and is used in the pigment kings' yellow; it is found, at times, native, but prepared artificially by passing dihydric sulphide gas through a solution containing arsenious anhydride. Thus it falls as a brilliant yellow powder, consisting of $As_2 S_3$. If this same plan be followed and the gas passed for some days through solution containing arsenic acid, a similar precipitate will be obtained, but composed of $As_2 S_5$, and known as sulpharsenic acid, or diarsenic pentasulphide.

Arsenic forms alloys with other metals, and, in so doing, it lowers their fusing point; but in all cases it renders them very brittle, even when combined in very small proportion. It is most destructive to the malleability of gold.

Discrimination of Arsenic.—1st, An acid solution will, if arsenic be present, give a yellow precipitate, on passing dihydric sulphide gas through it for some hours. This precipitate is nearly insoluble in hydrochloric acid, but soluble in alkalis or their carbonates, also readily in ammonia; and if the ammonia be evaporated off at a low temperature the arsenious sesqui-sulphide left may be reduced by heating in a tube after mixing it with black flux. Cadmic and stannic salts also give lemon-yellow precipitates with dihydric sulphide, but cadmium may be distinguished from arsenic by the sulphide not being soluble in ammonia; and stannic sulphide in not volatilizing on reducing with black flux.

2d. Ammonio-hydric sulphide produces, under the same circumstances, a precipitate of sesquisulphide; but if the solution be alkaline, or even neutral, a soluble double salt is formed—in fact, a sulphur salt, composed of arsenic sulphide with ammonium sulphide; and hence no precipitate. Acids will, however, throw it down, but diluted in colour from admixture of some free sulphur, separated from the alkaline sulphide also by the acid.

3. If ammonia be added to argentic nitrate its oxide will be precipitated; if the addition be then carried on until the oxide thrown down is nearly re-dissolved, we get in the clear liquid a solution of 'ammonio-nitrate of silver.' This is an excellent test, as it precipitates arsenious acid as an argentic arsenite—a beautiful lemon-yellow precipitate. This is soluble in nitric acid, and in ammonia; but as phosphoric acid will throw down argentic phosphate precisely similar chemical characters, this test must be trusted, only if others concur with it in giving evidence of the presence of arsenic.

4th. An 'ammoniacal sulphate of copper' (similarly made to the silver salt) will give an apple-green precipitate.

5th. If any solid matter contain arsenic, and it be mixed with a little black flux, dried, and heated in a glass tube, free from lead, we get a sublimate of dark grey metallic arsenic deposited upon a cool part of the tube.

6th. Arsenical compounds, when heated with a little sodic carbonate in the reducing flame of the blowpipe, give a most characteristic odour of garlic, due to the vapour of metallic arsenic reduced by the flux.

7. Reinsch's test depends upon precipitation upon a clean surface of metallic copper. The solution acidulated by hydrochloric acid, has a slip of copper put into it, and upon this if arsenic be present even in very minute quantity a grey film of metal forms. The slip is removed, washed in water, and then heated in ammonia, thus small scales separate which Fresenius says are 'not of

metallic arsenic, but cupric arsenide, and that if this substance, either simply dried, or oxidized by ignition in a current of air (which is attended with the escape of some arsenious acid), is heated, there escapes relatively but little arsenic, alloys richer in copper being left behind.'

But copper will similarly precipitate mercury, silver, lead, bismuth, cadmium, and antimony. None of these are volatile except mercury, and this may be distinguished from arsenic by its vapour condensing in metallic globules, while arsenic forms crystals of arsenious acid or anhydride.

8th. Marsh's test may be employed. It is founded upon the fact that arsenic will combine with hydrogen and form a combustible gas, from which the arsenic may subsequently be separated, by passing the gas through a tube heated to redness.

It is carried out thus:—A flask is fitted up for the evolution of hydrogen, and into this are put some perfectly pure dilute sulphuric acid and a few fragments of pure zinc—at least as far as to its contamination with arsenic. To the flask a small calcic chloride tube is attached, in order roughly to dry the gas. Then from the latter a small German glass tube is carried out and turned up at the end, the point being drawn into a jet. When the air has been driven from the apparatus, and gas escapes from the jet, the substance to be examined is introduced by means of the funnel-tube. Next, the gas may be lighted; and if a piece of cool porcelain be then brought suddenly down on the flame,

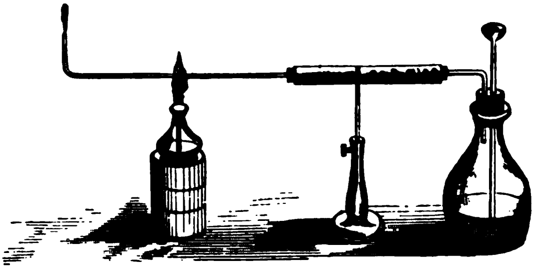

Fig. 84.

and quickly removed, it will have a deposit of arsenic formed upon it as a brownish-black spot; or the tube may be heated by a lamp, as in the drawing; when the gas, in passing this hot point, will be decomposed, and its arsenic deposited as a crust just beyond the hot part. This test is most delicate; and although the same result is obtained from antimony, the two may be distinguished, as the antimony spot is always of a dark blue-black, while that from arsenic is brown in colour. Dr. Guy has shown that the former is immediately dissolved when a drop of ammonic sulphide, in which a little sulphur has been dissolved, is added to it, the orange-coloured antimonial sulphide appearing as the ammonia evaporates. These effects do not occur with arsenic.

The presence of arsenic has often to be sought for in metallic copper, and for this Odling gives a very delicate and quick process in the *Journal of the Chemical Society*, vol. xvi. 1863, p. 248.

A few grains of the copper is cut in fine pieces, and put in a small tube-retort with excess of hydrochloric acid, and as much 'ferric hydrate or chloride' as contains a quantity of iron equal to about double the weight of the copper. It is distilled to dryness with care at last, to prevent spurting. The copper is thus quickly dissolved, and any arsenic carried over as chloride. This is condensed in a little water with excess of hydrochloric acid. The distillate may then be tested for arsenic by dihydric sulphide, or preferably by boiling in it a fresh piece of clean copper foil or gauze. In some cases the residue in the retort is again treated with acid and distilled, the distillate being added to the first one for testing. Odling further says, that most other oxygenants than ferric chloride gives rise to free chlorine, which passes over and renders the product unfit for immediate testing with dihydric sulphide or with copper. The ferric chloride used is freed from arsenic by evaporating once or twice to dryness with excess of hydrochloric acid.

Estimation.—In almost all compounds arsenic may be estimated as tersulphide. This is washed and dried at 212° F. and weighed; but if any substance is also present which would throw down sulphur from the dihydric sulphide, this addition would give too high an estimate. In such case the precipitate is oxidized by strong nitric acid, and the sulphuric acid so produced precipitated as baric sulphate, by adding baric chloride or nitrate. The baric sulphate is next weighed, and from this the weight of sulphur is calculated. This sulphur, deducted from the original weight of the sulphide, leaves that of the arsenic, which may be volatilized to prove the absence of any non-volatile metal.

By many chemists arsenic is not regarded as a metal, although it possesses the general characters of such; that is to say, it conducts electricity and heat, and has considerable metallic lustre. But its combinations with oxygen are both acids, and unite with bases to form salts in each case. At present we know of no basic oxide.

The applications of the metal too, as such, are very limited, the chief one being for alloying lead for the production of shot. It also lowers the fusing point of alloys considerably.

CHAPTER XVII.

IRON.

IRON has not only been known from the earliest ages, but its peculiar uses specified. It is mentioned in the Book of Job, and Moses speaks of 'an instructor of artificers in iron'—thus indicating that it was worked and manufactured as early as the sixth generation from the creation of the world; and its application to instruments of agriculture and of war is learned from the same sources. Its ores are very largely distributed, but those rich enough to be economically smelted are confined to certain districts. Its reduction is exceedingly simple, and more especially so when reduced from its oxides, for the mere heating of these in contact with carbonaceous matters suffices to reduce the metal, hence in early times its metallurgy was very simple. It is possible, too, that some small quantities may have been employed as found—in a native state—as such iron is very soft and pure. At the present time, specimens occasionally come to the hands of mineralogists. Meteorites are less pure than native iron; in them, it is invariably associated with nickel, and they also contain traces of cobalt, copper, and other metals. In the many specimens examined, the iron ranges from 67 to 94 per cent; the nickel from 6 to 24. Their masses generally range from a few pounds in weight to a ton or more. If cut, and the surface is polished, and then acted upon by nitric acid, a kind of etching action goes on; the acid acting on spaces between bands of untouched metal which cross the mass in two or three directions, and in these the nickel is more abundant than in other parts, for it is not equally diffused in the alloy. My friend, Mr. Terry, of Fulham, has a very fine collection in his cabinet, and in some of these, the marks above mentioned are particularly well shown.

Iron is universally present in nature, few substances being free from it: thus, even the human body contains no inconsiderable quantity, where it exists in the blood.

Native iron may be disregarded, as occurring in such very small amount as to be really but a mineralogical curiosity. Its chief ores may be classed as oxides and carbonates. Large amounts of sulphides exist, but these are not employed as sources of the metal.

The carbonates are the ores from which in Great Britain our iron is obtained; and as we are by far the largest producers, they may be said to be the most important ones. They are found in beds in the coal-formation, and alternating with layers of coal. Thus, in England, the ore and fuel are found at the same spot; and it may be remarked that the limestone employed as a flux is also equally near at hand, as also those peculiarly resisting clays used for fire material in the construction of our iron furnaces. Considering this, it will be evident that we have very extraordinary advantages in this manufacture, depending upon these facilities.

The ores may be considered in the order of the amount of iron they contain:—

1st. Magnetic oxide. This contains, when pure, 72·41 per cent of iron. It is found massive in enormous quantities, and occasionally crystalline in octohedra and dodecahedra. Swedish iron, which is excellent in quality, is chiefly obtained from this ore; and it is also found largely in Norway, and in the United States and Canada. In some localities it exists as a black shining sand, as at Taranaki in New Zealand, Nellore in India, and some other places. These sands furnish excellent steel, Wootz steel being produced from the latter. The Taranaki sand contains a considerable quantity of titanium, on which its steel-making quality is said to depend. Its composition is 3 atoms of oxygen, with 4 atoms of iron, or 1 atom of ferrous with 1 of ferric oxide. Specific gravity, 5·09.

2d. Specular iron ore and red hæmatite are both anhydrous sesquioxides. The latter, when pure, contains 70 per cent iron. The first, or specular ore, is common in Sweden and Russia, and also at Elba; and the second, hæmatite, in Cornwall and Lancashire, as also in France. The specific gravity of specular ore is 5·2, and of red hæmatite about 5·0.

3d. Brown hæmatite is a hydrated sesquioxide, which contains 14·44 per cent water, and, when pure, 59·89 per cent iron. The varieties of ochre, umber, and bog iron ore are similar ores: the two first contain clay and earthy matters, and the latter some ferric phosphate. The ores of France and Belgium are brown hæmatites, and Percy says that those exhibited by Belgium in 1862 averaged about 30 per cent iron. Specific gravity, about 3·9. The composition of the anhydrous sesquioxides is $Fe_2 O_3$, and of the hydrated, $Fe_2 O_3, 3 H_2 O$,

4th. Spathose iron ore is a crystalline variety of the carbonate; it is of a light brown or grey colour, and has a pearly lustre; it contains a large proportion of carbonates of manganese and of magnesia. When pure, it should contain 48·27 per cent. Composition, Fe, CO_3; specific gravity, 3·8.

5th. The impure carbonate or argillaceous ores worked in Great Britain are known as clay band and black band ores. The first is the ore of South Staffordshire and Wales, and it is also found in Belgium and in the United States; the second is found in the iron districts of Scotland, and, in addition to earthy impurities, contains an amount of coaly or bituminous matter, which often rises as high as 10 per cent, or at times higher. This gives it a darker colour, whence its name. It contains from 20 to 43 per cent, and the bituminous matter is serviceable as so much fuel in the smelting operations.

The average analysis of clay-band gives about 37 parts of protoxide of iron, 33 of carbonic acid, and 30 of earthy matters,—

these latter composed of lime, silica, alumina, and magnesia. This corresponds to about 28 parts of metallic iron.

The sulphides are classed under the name of pyrites, the most common one being a compound (more or less crystalline) of one atom of iron with two of sulphur; it varies in colour from white to a yellow,—at times so nearly resembling gold as to have led it to be mistaken for the latter,—a variety which is magnetic, and hence so called; it is always of a deep colour, and composed of 7 atoms of iron with 8 of sulphur. Ordinary pyrites is not used as a source of iron, but its sulphur is often employed in the manufacture of sulphuric acid, and also of alum. At times it contains a certain proportion of copper: this is worked by first separating its sulphur, and then smelting the copper.

The preliminary operation of estimating the value of an iron ore is done in the dry way, by a kind of miniature smelting process; it is performed in a good wind furnace, and at a very high temperature.

Percy* gives very full information upon iron assays. He says that, besides the ordinary wind furnace, a Sefstrom's or Deville's furnace may be used. The Swedish method of operating is in small brasqued crucibles (see p. 106): 10 grains of powdered ore are taken and mixed with the flux, of glass, lime, or other flux needed: this is done upon paper, by means of a spatula, or in an agate mortar. It is put into the cavity left in the centre of the crucible, and then covered with a plug of charcoal. The top is next luted with clay. Three or four crucibles may be placed on the stand in the furnace at one time; fuel is put round, but not on the top of them, and the fire lighted, the crucibles adjusted, and the furnace then filled up with fuel. In ten minutes, when the fire is fairly started, the top is opened to let out water and carbonic acid slowly from the ore. The furnace is then closed, and the heat raised to whiteness. In thirty to forty minutes the fuel will have burned down; the furnace is then opened, and the button and slag removed. The button is detached from the slag, and weighed, any detached grains being collected by the magnet and added for weighing. In Sweden this dry assay is often used in order that, from the fluxes found necessary, the proportions of materials needed for the blast-furnace charge on the large scale may be learned.

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* *Metallurgy of Iron and Steel*, page 237.

The fluxes recommended by Percy are—

1st. Silica in the form of pounded white quartz, or rock crystal, or clean white sand.

2nd. Glass. These are employed with ores which are deficient in siliceous matters.

3rd. China clay.

4th. Shale.

5th. Fire-clay.

6th. Borax glass.

7th. Lime, as free as possible from sulphate.

8th. Fluor-spar, which may be used instead of lime, it forms fusible compounds with silica or silicate. For the application of these, and the proportions to be employed, the reader is referred to the work quoted.

For the English method of assay 100 to 1000 grains of ore are worked upon. Supposing 500 are taken, it is mixed with about half its weight of glass, and rather more than half of dry lime, and about a fourth its weight of charcoal or anthracite in dust; and the mixture introduced into a Cornish, black lead, or French crucible, and luted up. The pot is then well placed in the centre of the fire, and the furnace quite filled with proper-sized coke. Until the aqueous portions of the mixture have escaped from the pot, the fire is kept at a moderate heat, after which the damper is opened, and the heat raised to its full extent, at which it is maintained for half an hour. At the end of this time the pot is removed, and tapped steadily upon the edge of the furnace, so as to shake all metallic globules through the slag, and bring them into one button below. When cold, the pot is broken, and the contents struck a few blows upon the side, which will detach the slag, and, if the operation has been successful, leave a clean button of metal, tolerably pure, or at any rate retaining about the amount of carbon in ordinary cast-iron. Thus it only remains to clean the button carefully with a scratch-brush, and weigh. If, however, the button is not well agglomerated, and the slag full of metallic beads, it is most probable that the heat has been insufficient, or that the flux was too small in quantity. Should this be the case, the slag may be powdered and the metal abstracted by a magnet, and added to the button to weigh; but if the button be very imperfect, it is better to make a fresh assay. In all these dry assays, the presence of manganese, titanium, or chromium, and also phosphorus or sulphur, may be recognised by practised eyes from the appearance of the slag.

The wet assay of iron ores is, in fact, an operation of analysis; but inasmuch as it is only the iron which is sought for, the ordinary operation of analysing the ore may be very much abridged by the simple estimation of the iron, after its precipitation as sesquioxide or ferric oxide, by means of ammonia.

This reagent is capable, to a great extent, of retaining in solution most metallic oxides, which are commonly associated with iron, but it must not be relied upon where very accurate analysis is required; for the iron precipitate is so gelatinous and soapy in its texture, that the other oxides are much masked and protected from its solvent action. Again, on the other hand, ammoniacal salts are capable of dissolving ferric oxide in a slight degree; and where certain organic bodies are present, the quantity so taken up is very considerable. While, lastly, as ammonia precipitates alumina with the iron, the separation of these two requires much care in manipulation.

The operation is carried out as follows:—A portion of the ore is powdered, and a quantity which may range from 20 to 50 grains is carefully weighed out. This is treated with 500 to 600 grains of aqua regia in a small flask, and heated to the boiling point. The clear solution is poured off, and the insoluble residue again digested with a second quantity of acid. The solution is again decanted, and the whole evaporated to dryness in a porcelain basin; the dry residue is redissolved in about 1000 grains of hydrochloric acid, composed of equal parts of strong acid and water. When the soluble part is taken up, the liquid is filtered, and to the residue in the filter the first insoluble residues are added, the whole washed, dried, ignited, and if its amount is required to be ascertained, weighed. The solution in hydrochloric acid is then made hot, and some ammonic chloride added, and then ammonia in excess. The heating renders the precipitate much less gelatinous and retentive; and at the same time more open to the action of the washing water, and the addition of ammonic chloride prevents any lime going down with the iron and alumina. The precipitate, which consists of alumina and ferric oxide, must be thoroughly washed, after which it is put into a beaker with a quantity of caustic potassa, and well boiled. This treatment having dissolved out the alumina, if any were present, the solution is poured off, and the precipitate undissolved again well washed. It is next dissolved in as small a quantity as possible of hydrochloric acid, and lastly, again thrown down by ammonia, washed, dried, ignited, and weighed. Every 100 parts of this precipitate equal 70 of metal.

This double precipitation by ammonia needed, from the presence of alumina in many ores, will assist in the retention of other oxides in solution, as they are thus subject to two digestions in the ammoniacal solvent.

If it be desired to learn the amount of lime and of magnesia in an ore, these are contained in the filtrate from the first precipitation by ammonia. To this latter, ammonic-oxalate added will precipitate the lime as an oxalate, which on moderate ignition is converted into calcic carbonate, the form in which lime was originally present in the ore. Lastly, from the filtrate from this lime salt, if magnesia was present, it may be thrown down by the addition of sodic phosphate. The precipitate of magnesic phosphate, formed after standing an hour or two, must be washed, dried, and ignited, and contains about 36 per cent of magnesia.

Of the several volumetric methods used, Penny's, by bichromate (or dichromate) of potassa, and Margueritte's, by potassic permanganate, are the most commonly employed ones.

Penny's depends upon the fact that a solution of a salt of chromic acid will, if added to a ferrous salt, with excess of hydrochloric acid present also, convert it into a ferric salt, the chromic acid becoming chromic chloride. The following is the reaction taking place :—$K_2\ Cr_2\ O_7 + 6\ Fe\ Cl_2 + 14\ H\ Cl = 3\ Fe_2\ Cl_6 + Cr_2\ Cl_6 + 2\ K\ Cl + 7\ H_2\ O$. And as we possess very delicate means of ascertaining the point in the addition of the chromic salt at which the conversion of the ferrous to ferric is just complete, we can learn the amount of iron by the amount of potassic dichromate required, presuming, of course, that its value in this way has been previously ascertained by testing it upon a known weight of pure iron. For this latter end good iron wire is used, which contains on the average fully 99·5 per cent iron, for only the purer forms of iron will draw well.

The solution of potassic dichromate should be made from pure salt, and a convenient strength is got by dissolving 76·25 grains in 1 pint of pure water, 1000 grains of this being equal to 10 grains of pure iron. Where this solution is stored, the vessel should, before using, have any condensed evaporated water in it mixed with the whole by shaking it up.

The test solution needed for ascertaining that the assay under examination is entirely peroxidized, is potassic ferridcyanide, and a very weak solution of this, viz. of about 1 grain to 5 ounces, is prepared. The operation is carried out thus: From 10 to 20 grains of the ore are heated in strong hydrochloric acid for half an hour in a flat-bottomed flask, the neck being closed by a funnel. When decomposition and solution of the iron compound are complete, it is diluted with water, and a few pieces of zinc are put in, and the liquid boiled until all colour is removed, or it has become of a very pale green, and it should contain no small particles of zinc. It is transferred carefully from the zinc to a porcelain basin, the residue washed, and also added. A porcelain slab is now prepared as a test-plate, by placing a number of drops of the potassic ferridcyanide solution in order upon it. Having filled a 1000-grain burette with the potassic dichromate solution, it is to be added by degrees to the iron assay in the basin ; and between each addition, after stirring, a drop is removed by a glass rod and added to one of the spots on the porcelain plate. As long as this produces any blue colour, it is an indication that ferrous salt is yet present unchanged; but as soon as no change takes place, the addition of dichromate is stopped, and the amount used read off the proportion of the 1000 grains will be just the proportion of 10 grains of pure iron contained in the specimen under examination.

The potassic permanganate for Margueritte's process may be prepared by heating in an earthen crucible 7 parts of potassic chloride with 10 parts of potassic hydrate to fusion; 8 parts of manganic dioxide (the common ore) are then gradually added, after which the mixture is heated for an hour until it assumes the condition of a friable unfused mass. This is removed, powdered, and digested in a flask with 100 parts of water (heated). When the mass is exhausted it is filtered, and the liquid neutralized with sulphuric acid; it is then evaporated for crystallization, and the crystals dried on a porous tile. Paper should not be employed, but the filtration is best done through a plug of asbestos or gun-cotton.

The use of the salt for iron estimation depends on the fact of its deoxidation by a ferrous salt, and the indication of this by loss of colour in the permanganate. The following formula of the reaction will explain the changes:—

$$2\ K\,Mn\,O_4 + 10\,Fe''\,Cl_2 + 16\ H\,Cl = 2\ Mn\,Cl_2 + 2\ K\,Cl + 5\ Fe_2''\,Cl_6 + 8\ H_2\,O.$$

Arsenic and copper interfere with the change, but they may be previously removed by zinc.

A solution of permanganate may be made of the strength of 50 grains to the pint of distilled water; if made from the pure salt, it will keep, with but slight change, for any length of time. A quantity of this is put into a 1000-grain burette, and the iron assay prepared just as for Penny's operation. The test-liquor is then passed in, stirring all the time. The red colour will disappear quickly at first directly the salt is added, but more slowly after a time. When this state commences, it is to be added very slowly, until at last the least trace of redness remains. Then stop and read off the amount of fluid used, from which the amount of iron may be calculated as before.

From the ores of iron already described, two kinds of products are manufactured (or we may consider three) differing mainly in the quantity of carbon they contain. These are known as cast iron, wrought or malleable iron, and steel. The second of these, or wrought iron, containing carbon in the smallest proportion, while the first, or cast iron, contains the greatest quantity, steel being intermediate as to its amount of carbon. They also contain silicon and sulphur, and sometimes phosphorus, but where these last are present in any quantity, they affect the quality of the metal very much.

Silicon is always present in considerable quantity in hot blast iron, or iron smelted with coke, and when largely so, the iron is inferior in quality. Its amount in pig-iron ranges from ¼ or ·25 per cent, up to 3·5 per cent, the grey iron containing most. Malleable iron contains generally about 1 part of silicon in 500. In steel its presence is never to any great amount. Henry, in his analysis of Indian Wootz (a particularly choice form of steel) estimates the silicon present at ·042 per cent. Half a per cent will render steel unforgeable. Sulphur is always more or less present in pig-iron, and when in any quantity diminishes its strength very much. Its average here is about 1·50 per cent, and its amount greater in white than in grey iron.

In malleable iron sulphur produces 'red shortness,' as shown by cracking under the hammer during welding, and less than 1 part in 2000 will produce this condition. Steel seldom contains much sulphur, and this may largely depend upon the fact that the better kinds of steel are produced from charcoal smelted iron.

Phosphorus in cast-iron acts much as carbon does, viz. it hardens it, and it also renders it more fusible. Its average quantity in cast or pig-iron is 1 per cent. Phosphorus in malleable iron renders it 'cold short,' that is, liable to crack when bent cold; one part in 2000 (about the usual quantity) does not injure it; ¾ or ·75 per cent will be very injurious, and such iron will show a coarse crystalline structure.

Silicon and phosphorus may both be derived from the ores, and the latter may also be introduced by the limestone used as a flux. Sulphur may result from the decomposition of pyrites present in the fuel, or from calcic sulphate in the limestone. The compounds which iron forms with carbon are metallurgically of all the most important, and looking at cast-iron, steel, and malleable iron, it will be seen how greatly the qualities and uses of the metal are controlled by the amount of carbon associated with it. But whether or not the carbon is chemically combined, that is, whether or not there exist definite carbides of iron, does not seem a very settled point. Karsten considers that in metal which contains a large per-centage of carbon certain carbides may exist, which are dissolved in excess of iron, for by his experiments he considered that 5·93 per cent was the largest amount of carbon which could be combined with iron. But Dr. Percy justly remarks that Karsten has not succeeded in separating carbide of iron from it. Iron containing much carbon constitutes cast-iron, and this carbon may exist in it in a combined state, or it may be in the condition of graphite or uncombined carbon. The fact that the carbon is in actual combination is shown on dissolving the metal in dilute sulphuric, or in hydrochloric acid, for the whole will then be soluble in it. But when the carbon is not combined, but in the state of graphite, the latter will remain as insoluble scales after the metal itself is in solution. Combined carbon produces white iron, and if uncombined grey, while a mixture of the two gives mottled iron. But a white or grey character, as also its granular or crystalline condition, are much influenced by the condition under which it has been worked, as, for instance, by the temperature at which it has been poured, the quickness or slowness at which it has been cooled down, &c. In mottled iron the substance will be white speckled with grey, where the white iron is large in amount compared with the grey. And it will be grey covered with white spots where the grey predominates.

White iron is always exceedingly hard and will resist the cut of a file much as hard steel will; but grey iron, where the carbon is uncombined, is soft, and approaches malleable iron in its capability of being worked.

The smelting of iron from its ores, where the latter are rich in quality may be carried out in such a manner and with such facility as to produce malleable iron at once from the ore. But the amount of carbon retained by the product varies much according to the ore and treatments employed, although it is never more than sufficient to produce a more or less steely quality of iron. Many ancient methods, and of late years many modern ones, have been described for the production of malleable iron thus directly from its ores, the ores employed, however, being chiefly hæmatites or tolerably pure oxides, and their treatment essentially consisting in heating them with carbonaceous matters.

In the Catalan method, which affords a good illustration of these operations, brown hæmatite is first calcined for two to three days, so as to disintegrate the ore somewhat, after which the finer portions are sifted out, the coarser being fit at once for smelting. This is affected in a small square or rectangular hearth built in brick, and with a solid bottom resting upon a stone base. Into the upper part of this hearth a moveable tuyere is carried so as to direct a blast downwards upon the contents. The blast is produced by descent of a column of water from a cistern with a fall of twenty to thirty feet.

In working, the hearth is first filled with heated charcoal up to the tuyere; this is then beaten down compactly, and the space above it divided into two halves by placing a sheet of iron from side by side. Into the half next to the tuyere charcoal is put, and into the other a quantity of lumps of calcined ore. The iron dividing plate is now removed, the blast put on, and the charge pressed down, occasional addition of the powder of the ore damped and of charcoal powder is made, and during the operation the blast is gradually increased.

The carbonic acid produced by combustion of the charcoal, in presence of so much heated carbon takes an additional proportional of carbon, and carbonic oxide results. This reduces the iron from the ore, which gradually subsides to the bottom of the hearth. The workman pressing it from time to time so as to bring it into a spongy mass.

The operation is carried out in about six hours, when a bloom or lump of spongy iron, weighing 2 cwt. or more, is lifted out, taken to a forge-hammer, and the slag or cinder hammered out. After which the metal is rolled into bars. It is apt to retain some slag in its texture, but is nevertheless very malleable, hard, and fibrous.

In working poorer ores, as also in localities where the smelting is carried out on such an extensive scale as is done in Great Britain, the iron is first converted from the ore into cast or pig iron by means of the blast-furnace. When wrought-iron is to be produced, this first product is subjected to operations called refining and puddling. And, lastly, steel was always formerly produced from decarbonized or wrought iron, by a peculiar process, called cementation, whereby a quantity of carbon is recombined with the iron. But of late years it has also been produced at once by decarbonizing pig-iron as run from the blast-furnace, as well as directly from the ore.

The first operation used in iron-smelting is calcination of the ore. For this several hundred tons, broken to a fit size, are arranged in alternate layers with small coal, a heap being so constructed upon the ground in open air, and commenced by a good thick layer of coal of about 1 foot thick, the layers of ore and coal being then carried up to 9 or 10 feet in height, and about 15 feet wide. The amount of carbonaceous matter required varies according to the nature of the ore. Thus clay ironstone will require a large proportion, rising to 20 per cent even, as it is almost entirely made up of earthy matters with the metal; but, on the other hand, black-band ores, which contain in themselves a large amount of coal-like matter, may be calcined with an exceedingly small addition of coal, when once lighted. Thus calcination, by expelling useless matters, concentrates the metal and leaves the ore porous; and in the case of the clay ores they will be thus raised from 30 to 55 per cent; and black-band from 33 to 65 or 70. Water and carbonic acid will first pass off, then sulphur from the pyrites contained in the ore will burn off, being thus converted into sulphurous acid or anhydride, by union with oxygen; and some ferrous oxide also by taking oxygen becomes ferric or sesquioxide of iron. The ore upon the whole loses about one-fourth its weight. The mound is always lighted on the windward side, so as to carry combustion inwards; and as it burns, more ore is often added at the far end until the heap becomes of very great length, and some months will thus be spent in the operation. It is at times performed in kilns, and not unfrequently dispensed with altogether, where hot blast-furnaces are used for the after-smelting operation.

The calcined ore is now ready for the blast-furnace. The common form of this is shown in fig. 85. It is formed by joining two truncated cones of solid brickwork at their bases; the longer one (*a*) being above and forming the body of the furnace. This and the short one under it (*b*), are built of good Stourbridge bricks internally; next, a casing of refractory sand, and, external to all, a thick coating of fire-bricks. The part, (*b*), called the boshes, is sometimes formed in fire-stone, a refractory stone found in the iron localities; for it is of much importance that this part be closely built, and of good standing material, as not only is the chief wear of the furnace upon this portion, but it has also to sustain the whole weight of the charge, amounting to some tons. Passing downwards, a square chamber (*c*) is formed below the boshes, also in fire-stone; this is the hearth and crucible. The

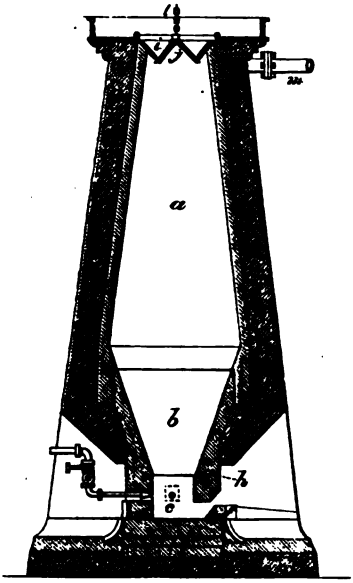

Fig. 85.

crucible being the portion behind the dam stone (*f*). The front of the hearth is not closed by stone as the three other sides are, but across the upper part only is placed a large stone (*g*), called the tymp; this is carried by an iron cross bearing plate the tymp plate (*h*). Underneath this is built in a large block of stone or fire-bricks called the dam (*f*), supported in front by an iron dam plate. In the top of this is a groove, the cinder-notch, through which the slag formed during working constantly flows, and runs down a sloped way called the cinder-fall.

The opening between the tymp and dam stone is stopped during working by ramming in a quantity of loamy sand. The

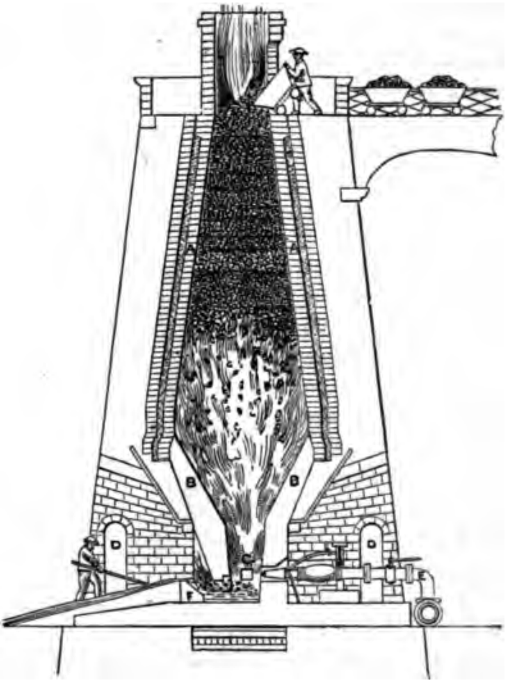

Fig. 86.

iron itself collects as reduced in the crucible, at the bottom of which is a tap-hole, which is kept plugged also with sand, and this is removed every twelve hours or so, and the collected metal run into pigs. Surrounding the hearth are formed arched galleries, D, fig. 86, which form passages for the workmen, and across these pass on three sides the pipes, or tuyeres of the blowing apparatus, E, whereby the blast is kept up.

Below all is a set of air-channels, as also an arched gallery passing into the centre, from the middle of each side; these serve to keep the furnace quite dry below, the former allowing the exit of moisture escaping from the brickwork itself.

At the top of the body is a short portion termed the tunnel head; this has three or four openings upon its side. It is surrounded by the gallery for the trucks which carry the charges of ore and fuel. The arrangement in layers of the charge and coal, which is scarcely maintained during work, shown in the drawing (fig. 86), are from Regnault, and the introduction of the workmen serves by comparison to give a very good idea of the dimensions of the whole arrangement, which is generally about 50 feet high by about 20 in diameter at the base; the widest part of the internal chamber being 15 or 16 feet. The whole structure is well tied together by iron bands externally.

The form of the blast-furnace varies much in different places, and is governed somewhat also by the nature of the charge to be smelted, both as to the kind of fuel, and of ore. A main object is the adoption of such a shaped body as shall allow of the regular descent of the charge, and also to have the boshes and hearth of sufficient strength and fit shape to sustain the great weight of the charge at the high temperature to which it is subjected. Percy gives a most extensive set of drawings and descriptions of blast-furnaces,* commencing with Mr. K. Blackwell's furnace in use at the Corngreaves Iron Works; he gives this as 'a typical illustration of a modern English blast-furnace.' In this latter there appears no fixed point at which the body could be said to end and the boshes commence, but the whole 'shaft' is bounded on each side from bottom to top by a steady curved line.

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* Percy's *Metallurgy, Iron and Steel*, page 351.

The blast to these furnaces is generally supplied by a large cylinder (*a*) fig. 87, of about 8 feet diameter by 9 or 10 high. In this a piston (*b*) is worked by its piston-rod passing through a stuffing-box to connect with the beam of a steam-engine. As this piston begins to ascend, it draws open a set of inlet valves placed below, and thus the space below it fills. In rising it forces the air from above it by a valve opening into a large air-main, at the same time closing the air-admission valves formed at the top of the cylinder. On the return down stroke, the under admission valves are first closed and the entry to the air-main opened, thus the air below the piston is passed in, while at the same time the upper main valve is drawn close, and the entry valves above opened for a fresh upper supply. By the succession of these actions a continuous supply is thrown into the iron main, which is of large dimensions, in order to equalize the blast. The furnace is said to be a cold-blast one when the air is sent in at ordinary temperatures, but hot-blast when the air is heated up previous to passing it in. For the latter kind the air is sent through the heating apparatus, and thence by the tuyeres to the furnaces themselves.

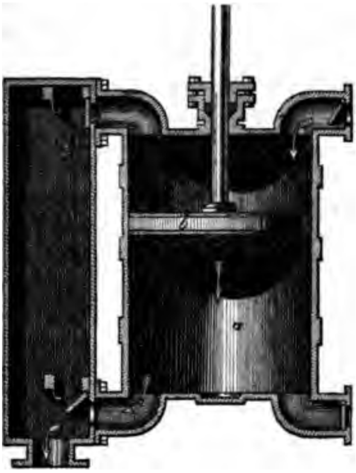


Fig. 87.

The tuyeres are tubes of cast-iron, but as these would be liable to fuse at the furnace entry, especially when carrying in a hot blast, they are surrounded by jackets, through which a stream of cold water flows by means of inlet and outlet tubes; these tuyeres are shown at (*d*), figs. 88 and 89, where they are applied to the refinery. In the blast-furnace the tuyeres are so arranged as that the blasts they deliver shall not meet, and so interfere with, or check each other. These water tuyeres occasionally become leaky, and if this occurs to any great extent, dangerous and fatal explosions may occur, for the escaping water passes on to the hot metal in the crucible, and the sudden generation of an immense volume of steam will then blow out the contents of the crucible and of the lower part of the furnace by the front opening. The heating of the blast is effected in a variety of ways. Sometimes by passing it through iron tubes heated up by a furnace; these are called pipe or tube ovens. In other works chambers or ovens are employed, which are heated by the combustion of the waste gases collected at the tunnel head of the blast-furnace. By such means the blast is heated to degrees ranging between 600° and 800° F., or 315° and 426° C.

Siemens has increased the temperature of the hot blast by employing his regenerative chambers (page 79), and heating these by the waste gases of the blast-furnace. Two chambers (just as in the steel-furnace, fig. 13) are used; the gas is first burned in one, and after it is heated up, the air for the blast is passed through it, the gas meanwhile being turned into, and burned in the second. By the time the first has parted with its heat to the air the second is ready for use in the same way; the course of the gas and air is therefore changed in them, and this alternate working of the chambers will maintain the blast at 1200° to 1300° F., or 648° to 704° C., and by means of waste gases which would otherwise have passed away. The economising of these gases has given rise to several plans for their collection at the tunnel-head of the blast-furnace. Of several, a very good plan is shown in fig. 85, where (*i*) is a large cup partly closing the whole top of the furnace; rising up to this, by a chain and balance, is a cone (*j*). On throwing in the furnace charges this latter falls, and after entry of the materials, rises again by the counterbalance, to close the cup. The evolved gases are then carried out by the large tube (*m*) to their use elsewhere.

Mr. E. A. Cowper has devised an excellent form of stove for heating the blasts, where a temperature is given to it exceeding even that of a red heat.

The fuel employed in England is always either coal or coke. Until about the year 1720 charcoal was exclusively burned, but from that time till 1780 coal gradually became generally used, its introduction being slow, but mainly assisted by the employment of the powerful blowing machines above described.

In Sweden and Austria charcoal is used; and hence, from the absence of sulphur in the fuel, the Swedish iron is much prized for steel-making by cementation.

By the cold blast, iron is produced of extreme tenacity and strength; and this brought about the employment of coke, which is rendered necessary with the cold blast, and which in itself is a purer fuel than raw coal. But when it is stated that between two and three thousand cubic feet (and often much more) of air are thus thrown into one of these furnaces per minute, it will be evident that such a body of cold air has a great tendency to bring down the temperature of the furnace; and this is now proved by the saving of fuel effected when the supplied air is previously heated up. This saving is enormous, especially when the fact is taken into the calculation that by this employment of heated air raw coal is sufficient, because the action of the fuel and ore takes place lower down in the furnace, that is, nearer to the tuyeres, and therefore so large a body of hot fuel is not required in the upper parts of the furnace. Hence, in Scotland alone, it is calculated by a late writer upon this subject that no less than two millions of tons of coal are saved annually. The hot blast was introduced at Glasgow in 1828. Percy gives a comparison of hot and cold as to economy, and states that at the Clyde works, in 1829, for a weekly make of 110 tons, 14 cwt. 2 qrs. of iron by three furnaces, the average consumption of coal per ton was 8 tons 1 cwt. 1 qr. (used as coke); while in 1833, at the same works, with the hot blast and coal used, for a weekly make of 245 tons, the average consumption of coal was only 2 tons 5 cwt. 1 qr. per ton.

That the condensation of the air, and consequent amount of oxygen contained in a given bulk, has much influence, must at once be evident when the quantity employed, as just stated, is borne in mind; and this is further shown in the difference found in the quality of the product, according as it may have been smelted in winter or summer, or in moist or dry weather; for in dry, frosty, winter weather the quality of iron is said to be better than that of iron produced in warm, moist weather.

The great object of the iron-smelter, in selecting a fuel, is to avoid the presence of sulphur; and it is the impossibility of obtaining coal or coke free from sulphur which gives charcoal-smelted iron the great superiority.

Calvert has proposed, in order to get rid of sulphur, to add small portions of sodic chloride, injecting it into the blast. This, by acting upon the ferric sulphide contained in the coal, decomposes it, and forms sulphur-chloride, and it is found that iron so made more assimilates charcoal-iron. Calvert adds the salt, to the extent of 1 to 2½ per cent, to the coal before it is coked, or else mixes it with the coal-charge for the furnace.

Then as to flux. If the ore were smelted without any, the silica contained in it would retain much of the metal, forming with it ferrous silicate. The use of a flux, then, is to unite with the silica, so as to set free the whole of the iron; and, therefore, care is required that a sufficient quantity is present for this end; but, on the other hand, it must not be in any great excess, or the slag will not be sufficiently fusible, and so, hanging about the charge, the metal will not readily subside.

Limestone is the flux usually employed, which becomes lime at the temperature of the blast-furnace; and a slight excess is not injurious, for it will combine with any sulphur present, and assist in its removal as calcic sulphate. The purest limestones are those best adapted for iron fluxes; for, although those containing magnesia or silica form more liquid and separable scoriæ, yet the presence of these bodies injures the quality of the iron.

Now the working of the blast-furnace is as follows:—Supposing it to be a new one, heated up for the first time, or 'put in blast.' A quantity of wood is first put in, and upon this small portions of ore and flux alternating with fuel are then thrown in, and the blast sparingly put on. This is done for the purpose of gradually bringing up the heat, for, if effected in a sudden manner, the furnace would crack and become injured. Next, the regular working begins, and this is subject to variation as to the mixture operated upon, fuel, amount and strength of blast, &c. to be employed; these, again, being dependent upon the nature and associations of the ore, kind of fuel, &c. But the following details may be given as an example :—

Supposing the ore to consist of equal quantities of clay and black-band calcined together, to every nine hundredweight, about two hundredweight of flux is added, and well mixed with it. This mixture will require nearly half a ton of coal. Every hour a portion of coal is first wheeled in and emptied at the throat of the furnace into the body, and upon this a layer of ore and flux is thrown, then another of coal, and a second one of ore, and so on in the same order until the body is filled. Indeed the subsidence of the charge is an indication as to when replenishing is needed; it is gradual, and occupies about forty hours or more in passing down; thus it will be found that a large furnace will in 24 hours absorb 37 tons of material, and in the same time yield about 7 tons of pig iron. The furnace is tapped every 12 hours, and the metal allowed to flow out in front into a bed of sand, wherein moulds are formed, being simply oblong semicylindrical cavities, which deliver corresponding bars or masses of metal, technically termed 'pigs.'

A well-built furnace will last some years, often five or six, without needing blowing out for repair.

The quantity of air injected by the blast-engine must be carefully regulated so as to maintain efficient combustion, and experience of the working of the particular furnace is needed to decide the amount. It is usually sent in at a pressure of 3 or 4 lbs. on the inch, and by a steady non-intermittent stream. This latter point is ensured by the employment of very large air-mains, as before stated.

The reactions of the blast-furnace are briefly as follows :— During the operation the combustion of the fuel being carried to the utmost, by the oxygen derived from the air thrown in by the blowing apparatus, the intense heat thus generated drives off all moisture, volatile gases (the carbonic acid of the flux thus passes off, and also the nitrogen of the decomposed air), these escape at the throat of the furnace. The carbonic anhydride formed by the combustion of the coal, in passing through the heated fuel, takes another proportional of carbon, and becomes carbonic oxide, itself a combustible gas. One volume of carbonic anhydride thus affords two volumes of carbonic oxide, and during this change the temperature at the point of its occurrence, viz. the lower part of the boshes, becomes much lowered. The carbonic oxide, in company with hydrogen compounds, also derived from the decomposition of the coal, together react upon the ore, action being facilitated by the large surface afforded by its being in a thoroughly spongy condition. Thus the ore is reduced, being changed from ferric oxide into magnetic oxide, and at times into metallic iron. This takes place in the boshes, and is quite completed as it fuses and passes down, having subsided with the flux into the hottest part of the furnace. Here the iron combines with a portion of the carbon of the fuel and sinks down through the slag as cast-iron, being protected from the action of the blast, by a thick layer of slag, for it would otherwise be liable to be oxidized, although its surface is now below the tuyeres.

The scoria or slag is allowed to flow out by the cinder-notch during the operation over the dam-stone, and when cold is broken up and taken away, or at times cast into slabs for building uses. Or it may be received in a truck formed of iron with moveable sides, thus it is cast into a square block, which may be removed in one mass on taking off the truck sides; these trucks are termed cinder-tubs.

These slags, termed blast-furnace cinders, are actual salts, wherein the silica acts as an acid, and the lime and similar constituents of the flux form the base. They are commonly of a brownish yellow, or of a grey colour, often with a tinge of blue or green. Two analyses may be given as specimens of their usual composition. The first is one by Percy on the slag from 'Messrs.

Blackwell's hot-blast furnaces working with coke.' The second is an average of thirteen analyses made by Riley at Dowlais, and also taken from Percy's *Metallurgy of Iron*, p. 499:—

	1.	2.
Silica	37·91	43·07
Alumina	13·01	14·85
Lime	31·43	28·92
Magnesia	7·24	5·87
Protoxide of Manganese	2·79	1·37
Protoxide of Iron	0·93	2·53
Potash	2·60	1·84
Sulphide of Calcium	3·65	Calcium 1·01 Sulphur 0·89
Phosphoric Acid	...	traces
	99·56	100·35

The gases evolved from the blast-furnace have been the subject of much careful investigation by Tunner, Ebelmen, Schafaeutl, Bunsen, and Playfair, and others. It has already been shown that they are utilized as sources of heat by their combustible qualities; although, as will be seen, more than half their bulk is made up of the non-combustible gas nitrogen, which is separated from the decomposed air of the blast. The inflammable gases are carbonic oxide, hydrogen, marsh gas, and olefiant gas, with a small quantity of cyanogen.

Out of the number of published analyses, those by Bunsen and Playfair, made at a furnace at the Alfreton works, may be given. This furnace was 40 feet high. It was worked by hot blast, and coal, the blast having a temperature of 626° F. = 330° C., and a pressure of 6·75 inches of mercury. The ore was calcined clayband, and of this, 420 lbs., with 170 lbs. limestone flux, were worked with 390 lbs. coal. These quantities were thrown into the furnace every 20 minutes, and the produce of this amount was 140 lbs. iron. The following were the analyses of the gases collected at the various depths down the furnace below figured:—

Depth from Top.	Nitrogen.	Carbonic Acid.	Carbonic Oxide.	Marsh Gas.	Hydrogen.	Olefiant Gas.	Cyanogen.
5 ft.	55·35	7·77	25·97	3·75	6·73	0·43	0·00
8 „	54·77	9·42	20·24	8·23	6·49	0·85	0·00
11 „	52·57	9·41	23·16	4·58	9·33	0·95	0·00
14 „	50·95	9·10	19·32	6·64	12·42	1·57	0·00
17 „	55·49	12·43	18·77	4·31	7·62	1·38	0·00
20 „	60·46	10·83	19·48	4·40	4·83	0·00	0·00
23 „	58·28	8·19	26·97	1·64	4·92	0·00	trace
24 „	56·75	10·08	25·19	2·33	5·65	0·00	trace
34 „	58·05	0·00	37·43	0·00	3·18	0·00	1·34

These numbers represent the volumes of the respective gases, contained in 100 of the mixed ones, collected at each depth figured.

That potassic cyanide is largely produced in blast-furnaces has long been known. It is formed by union of nitrogen with carbon, which takes place in presence of potassium; the latter being derived from the ash of the coal, and also from the clay of the ore. The salt was collected from the Alfreton furnace in large quantities; and as for every 100 parts of coal, 0·778 of the salt is found, Bunsen and Playfair calculated that in a day's work of the furnace they used, 224·7 lbs. of potassic cyanide was formed. They consider that it assists in the reduction of the iron.

The pigs of iron thus obtained from the blast-furnace are actually cast-iron, but in addition to the requisite quantity of carbon, they usually contain a varying quantity of silicon; the carbon ranging in quantity between 4·8, and as small an amount as 1·5; the silicon between 4·7 and 0·65. Pig-iron contains also some sulphur, as also phosphorus, very frequently manganese, as the ores of that metal often accompany those of iron. It may also contain titanium, and occasionally copper, arsenic, cobalt, and chromium. Ninety per cent may be taken as the average quantity of iron contained in ordinary pig.

For moulding purposes it is at once ready for use; but it varies much in quality; this being determined by the nature of its fracture: thus the smelter classes it as No. 1 to 4. By the appearance of its fracture, No. 1 gives a grey, or black and soft metal, being the best quality of cast-iron; this has a specific gravity of about 7·1; No. 2, mottled; No. 3, white, whose specific gravity averages 7·5; and last, No. 4, called silver iron, being the lowest in quality. The two first qualities are at once ready for the founder's use, hence they are often called foundry iron, and the latter forge. This is the practical division, but at least eight varieties may be distinguished between the No. 1 (grey), and No. 4 (silver iron).

The greater the amount of carbon the more fusible the metal will be. Its average fusing point is 2786° F. = 1530° C. The iron-founder for remelting chooses a higher carbonized iron for the above reason, for it is sure to refine somewhat in his furnace, and in so doing to become less fusible. Iron, besides its other advantages, is most useful for castings from its expansion on cooling, causing the casts to become very sharp.

There is a form of white cast-iron, which has come into much use, from its great service in the Bessemer process, where it is employed to furnish the carbon required to convert the purified iron into steel. It is smelted in Germany from spathose ores, which contain a large proportion of manganese; at times as much as 12 per cent. It is known as Spiegel-eisen, or mirror iron, from its exhibiting brilliant tabular crystalline surfaces. From the quantity of carbon it contains, it is very fusible. The third analysis here given shows the principal constituents of Spiegel-eisen taken from a very complete analysis made by Fresenius. With it are two cast irons. The first is that of grey French charcoal iron which had a specific gravity of 7·0; it was analyzed by Abel. The second is one of white Silesian crystalline iron, of a specific gravity of 7·531, and also by Abel.

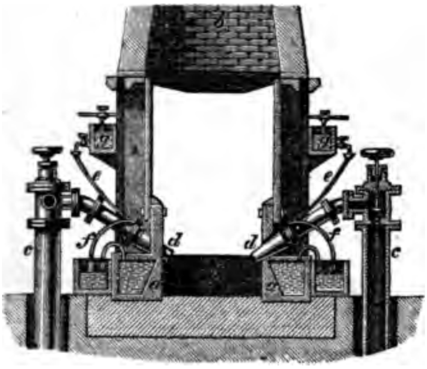
	1.	2.	3.
Combined Carbon . .	...	4·94	4·323
Graphite . . .	3·40	...	
Silicon . . .	0·80	0·75	0·997
Sulphur . . .	0·05	trace	0·014
Phosphorus . . .	0·45	0·12	0·059
Manganese . . .	...	5·38	10·707
Copper . . .	...	0·24	0·066
Arsenic . . .	a trace	...	0·007
Cobalt . . .	...	a trace	trace
Chromium . . .	a trace	...	...
Iron . . .	95·18	88·57	82·860
	99·88	100·00	Minute quantities of other Metals estimated making up the 100 parts.

The operations already detailed are all that are required for the production of casting metal; but when it is desired to render the iron malleable, or, in other words, to produce wrought-iron, it is subjected to certain chemical and mechanical operations, which may now be described.

The first of those is technically termed 'refining,' and is performed in 'running out fires or refineries.' (Figs. 88 and 89.) These are small furnaces built up of hollow metal sides (A and *a*), the upper ones (A) carry the chimney (*b*), the lower ones (*a*) surround the hearth on three sides, and are kept cool by a quantity of water circulated through them. The chimney (*b*) is about 18 feet high. From the air-mains (*c*) the tuyeres (*d*) are made to point downwards so as to direct their blast upon the surface of the melted metal upon the hearth; they are kept cool by water-jackets supplied by the pipes (*e*), and the water is carried away by (*f*), *g g* are the water cisterns. The hearth (*h*, fig. 89) is about 3 feet by 2, and 2 feet 6 inches deep. Six blast tuyeres are here shown. A shallow mould (*i*) is placed in the front. This is a hollow plate kept cool by the circulation of water under it, and also further protected from the hot metal by being lined above with loamy sand.

In operating, the hearth is first filled with coke, upon this are next laid about six pigs of blast-iron; and lastly, these are covered up in coke. The fire lighted, a moderate blast is put on; the metal melts and subsides to the bottom; and as the coke now burns away more is supplied so as to keep up the fusion of the iron. In this way the greater portion of those impurities, which were essential in obtaining the blast-iron, are burned out, for in the case of malleable iron these are the elements which destroy its tenacity and strength.

Fig. 88.



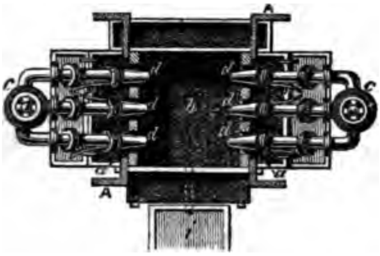


Fig. 89.

The bodies thus got rid of are a large portion of the carbon, nearly all the silicon, phosphorus, and some sulphur; but in order to get the product as free as possible from the latter, it is necessary, in place of coke as a fuel, to employ charcoal, for the former always contains more or less sulphur.

The metal bubbles up much during the operation, quantities of carbonic oxide are given off and assist the combustion, the silicon of the metal is first oxidized, and the silica so formed unites with a certain portion of oxide of iron, so that in the end the product is generally found to be about one-tenth less than the metal employed, and the scoriæ separated are found to consist of ferrous silicate, with other impurities. This slag is called 'finery cinder.' Some analyses of this are given by Percy;[*] one of these, made by Riley, of 'refinery cinder of the ordinary kind,' gave—

Silica	25·77
Protoxide of Iron	65·52
Protoxide of Manganese	1·57
Alumina	3·60
Lime	0·45
Magnesia	1·28
Sulphur	0·23
Phosphorus	1·37
	99·79

Refining thus requires about two hours for completion, at the end of which the metal is run off upon the mould so as to form plates of about two inches thick; these are rendered brittle by suddenly throwing a quantity of cold water upon them while hot, after which they are broken up for the next operation.

For tin plate-making very pure iron is required, and hence this operation is always carried out for such metal with charcoal as a fuel. The metal is then first melted, and afterwards run into the charcoal fineries; and when the furnace operation is over, in place of running the metal out into plates, balls or blooms are removed and taken to the hammer, by which the remaining finery cinder is driven out.

In running the metal as first described, the finery cinder also flows out; by its lower gravity this comes to the top of the cast plate, and its detachment from the metal is facilitated by the water thrown upon it. Regnault gives the following analyses of metal before and after refining (*Chimie*, vol. iii. p. 96):—

	Before.	After.
Carbon	3·0	1·7
Silicon	4·5	0·5
Phosphorus	0·2	0·0
Iron	92·3	97·8

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[*] *Metallurgy of Iron*, page 627.

The operation of puddling, originally devised by Cort, is a supplementary one to refining; and indeed is often carried out upon the metal without previous refining. It consists in heating it out of contact with fuel, and when in a state of fusion, stirring it in such a manner as to bring the charge well in contact with atmospheric air, whose oxygen combines with the carbon, and other impurities of the cast-iron. It is carried out in a large reverberatory furnace (figs. 90 and 91) having a somewhat oval bed of about 6 feet by 4 at its widest part. In modern furnaces this is formed of iron, and is set hollow or upon columns, so that by the air space below it is prevented heating up too much. Its upper surface and sides are protected by being covered with a layer of ground slag and oxide of iron worked on; and at the flue end of such furnaces the bed narrows and has a low brick ridge raised upon it. This is not more than 2 or 3 inches high, and is for the purpose of preventing the metal passing down, as there is a rapid fall at B, towards the floss hole, C. This fall is to get rid of the slags formed, which are removed at the latter hole. At this end a chimney, D, is carried up for about 50 feet, at the top of which a damper is fixed, capable of regulation by means of a lever and

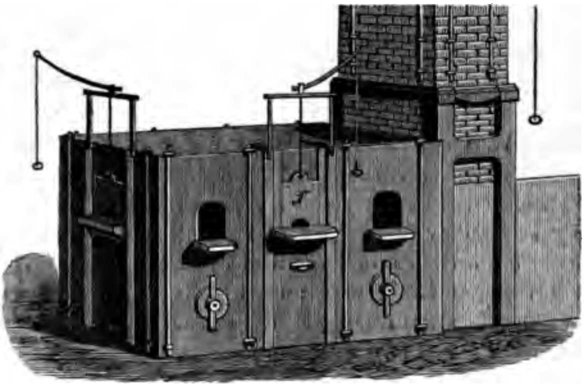

Fig. 90.

chain by the workman below. The bridge, E, between the furnace and reverberatory bed, is high. The furnace itself is large, the fire-place being about 3 feet × 4. It is fed and regulated by an opening in front, or else by one on the working side at G. The opening (*f*, fig. 90) is the one whereat the puddling of the metal is carried on, consequently its door is slung to the frame seen above it, so as to be readily drawn up. Lastly, the opening, H, serves for charging in the metal, as also for cleansing the bed.

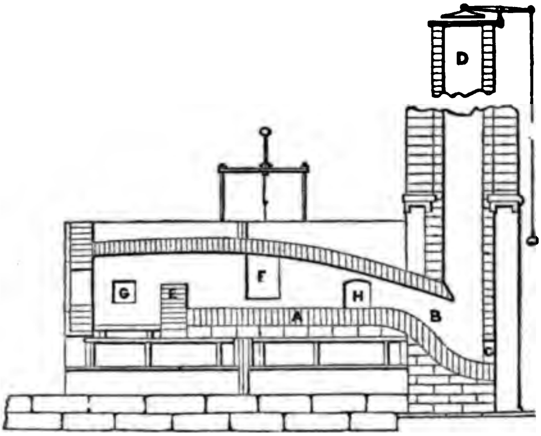

Fig. 91.

Upon the sole of the furnace a charge of about 4 cwt. of broken plates of refined iron is placed, at times associated with portions of unrefined, or the crude iron itself may be puddled without undergoing the refining operation. In puddling refined iron alone, often termed 'dry puddling,' it is customary to add a certain quantity of oxide of iron, equal to about one fourth the weight of iron to be worked, in the form of scales from the forge; these afford oxygen to the carbon, for in this case the carbon existing in the metal being in much smaller quantity, there is less action set up by the escape of gas, and thus less atmospheric action, so that the addition of some oxidizing agent is rendered necessary. The metal is piled up round the sides, leaving the centre of the bed clear. The fire is then made up, and the draught increased by closing the door and opening the chimney damper. The metal is at the same time moved about so that in about half-an-hour it begins to fuse and settle down on the sole of the furnace. The heat is now moderated and the metal kept stirred. A brisk evolution of carbonic oxide takes place from the whole surface, as the mass becomes sufficiently fluid to allow of its ready escape, giving it the appearance of boiling up. The puddler now introduces a long-handled paddle by the working door and stirs the gas as much as possible out of the mass. The combustion of this carbonic oxide assists in heating the charge, for it burns all over the surface as it is evolved. Its production is kept up by union of the carbon of the metal with the oxygen of the iron scale. He next works the metal sufficiently out of the strong heat to cause it to assume a doughy consistence, the fire being at the same time lowered to just the point at which it suffices to keep it in that state. It is then constantly worked about with the paddle, so as to assist the escape of the last portions of carbonaceous gases, and thus, as the metal refines, it becomes less fusible, until at last it acquires a sandy, granular state, or 'comes to nature.' The heat is now so far increased as to keep the balls of metal, into which the puddler has worked the whole charge, coherent, or, as he would say, 'heavy.' In fact, as the carbon has been separated from the metal, so has the fusing point risen, and increase of heat is therefore needful in order to keep the charge soft enough for working. Then, on the other hand, from time to time a small quantity of water is thrown into the furnace, when it is found needful to lower the working temperature.

When unrefined iron, or the pig as it comes from the blast-furnace, is operated upon, the charge is much more fusible, and from the same cause, viz. the greater amount of carbon present; the effervescence or boiling will also be greater: hence this process is often called 'pig-boiling.'

At the close of the operation the workman gathers as large a ball as he can readily lift on his paddle, and, placing this upon the hottest part of the hearth, squeezes out as much of the scoriæ as he can so separate, repeating this upon the whole furnace-charge. The heat is again raised, and the balls, or blooms (which weigh about 80 lbs. each), are taken out in succession for mechanical treatment, for which removal they are lifted by an iron rod, or 'porter,' pressed into their substance.

The mechanical operations are squeezing, or else hammering (or 'shingling'), or rolling by puddling-rolls: thus the blooms are elongated, and puddled bar is produced. This is then cut up, welded together, and again rolled, in order to convert the granular texture of the metal into a fibrous one, which is the characteristic of all well-manufactured iron. Thus merchant bar, or No. 2 iron, is produced; and if this cutting up, welding, and rolling, is again performed, No. 3 iron results.

The squeezing operation was performed by massive iron jaws (hence the apparatus is called an 'alligator'), or else by some form of rotating squeezer; but these have given place to the hammering operation, or 'shingling,' which is now generally effected by a Nasmyth's or Condie's steam-hammer. In the ordinary steam-engine the cylinder is actually the fixed part, the piston-rod moving up and down in the former, being the first moving agent of the machine. In the forge-hammer, however, known as Condie's hammer (which, like Nasmyth's, is actually the cylinder arrangement of an ordinary steam-engine), the piston-rod is firmly fixed in a massive framework, while the cylinder itself moves up and down upon this rod during work; the cylinder, being exceedingly massive, serves then as a hammer, and is made to act upon a large anvil placed below, and in its axis. For forge purposes these cylinders have been made of 6 to 7 tons in weight, and with a stroke of 7 feet or upwards; but for 'shingling' purposes they are usually from 2 to 3 tons.*

For carrying out these operations, the puddler lifts out of his furnace a mass of from 60 to 80 pounds weight, being, in fact, as heavy a ball as he can collect and work: taking this upon the end of his rod or porter in a thoroughly hot state, he places it upon the anvil: the hammer, then being set in action, hammers or rather squeezes out the still fluid slag, and condenses the purer metal. Watching this operation, as done at Wednesbury upon some puddled blooms, the workman first hammered upon the flat sides, turning them about and employing a kind of squeezing blow: thus a fluid slag was driven out in all directions. The bloom was then set up end-ways, by which more was separated; and after this the blows were increased in speed and force, so as to condense the mass.

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* The steam forge-hammer employed by Krupp at Essen weighs fifty tons, this works on an anvil face of 180 tons, the latter supported by 1040 tons of cast-iron in eight blocks: a total weight of 1270 tons.

The blocks so obtained are then passed through grooved rollers (of about 18 inches diameter by 5 feet long), so as to lengthen them; these bars are then cut up (as before stated) and fagotted together; and the oftener this is repeated the more fibrous will be the texture of the product. By means of these first rollers much scale will be separated from the heated metal; this is washed away by the stream of water which is kept flowing over the rollers in order to keep them from heating by contact with the hot bars. The workman moves the metal to the rollers by tongs, and the slight roughening of the latter causes them readily to seize upon the mass and drag it through. Lastly, by passing the metal through finishing rollers the form desired is given to it, as round rods, square or other bars, or such forms as T-iron, angle-iron, railway-rails, and others.

After the removal of the blooms from the puddling furnace, the slag or scoriæ are cleared out. This, like the 'refinery cinder,' is an iron silicate, containing also some iron phosphate and sulphide. They contain from 50 to 60 per cent of iron, and are sometimes reserved for reduction by means of lime as a flux; but the iron produced from them is of very inferior quality, and always cold short.

In welding puddled bar for conversion into merchant iron, the heating is performed in a reverberatory furnace, where they are heated to just a welding heat, air being carefully excluded, which, if admitted, would tend to prevent cohesion by oxidizing the surface. For this object the openings are carefully placed, and the one for introducing and withdrawing the bars is placed under the shaft and at the back of the bed. Thus any rush in of cold air takes a course into the flue, and does not pass over the heated bars on the bed.

There is now much demand for large plates; and the size of these, as produced by rolling, is something astonishing. Thus in the Exhibition of 1862, amongst others, was an armour-plate rolled by J. Brown & Co., which measured 21 ft. 8 long by 4 ft. 2 wide and 6½ inches thick: it weighed 10 tons 12 cwt.

In the process of puddling, just described, it will be seen that the separation of impurities from the crude iron, although effected by atmospheric oxidation, yet requires much labour on the part of an operative, who must possess also a large amount of skill and judgment, without which the iron produced will not be of good quality. Hence many schemes have been devised to do away, to a great extent, with manual labour; and, indeed, the Bessemer operation, by which steel is now largely produced, took its origin in the attempts to produce malleable iron by blowing air through the fused crude metal. But puddling operations are still carried on as before, and the chief improvements relating to them are those for the utilization of the waste heat from these large furnaces, which is now much employed in heating the boilers of steam-engines on the works. And, again, Siemens has much improved the furnaces themselves, by employing gaseous fuels, and his regenerators, in place of the solid fuel always formerly employed.

STEEL.

Steel is simply iron chemically combined with just the amount of carbon which will give it its extreme amount of toughness and hardness, without being sufficient to render it brittle in itself, while at the same time a condition of metal is produced, wherein yet increased hardness and brittleness can be given to it by the mechanical means of heating, and then suddenly cooling; and further, admitting of the original amount of softness being restored by again heating and slowly cooling. And another characteristic property of iron carbonized to the condition of steel is its power of permanently retaining magnetic properties if conferred upon it.

In truth, the relative proportion of carbon contained in iron (supposing the metal comparatively pure as regards other deteriorating agents) seems entirely to control the quality of the metal, and the more completely it can be refined from it, the softer and more malleable will be the product.

Then, as to the actual amount of carbon producing the different forms of iron and steel; starting from the best kinds of iron, such as can be employed for drawing fine flexible iron wire, for example. This would be found to contain not more than 0·12 per cent carbon.

Between this and steel would come ordinary malleable iron, containing about 0·2 per cent, and next we may place steel; and from older analyses the following results may be given :—First, Mushet found in soft steel, 0·833 carbon; in ordinary steel, 1·00; in ordinary hard, 1·11; and in the hardest, 1·67 per cent. Berthier gives the amount in ordinary English steel as 1·87. But in later analyses, given by Siemens (see *Jour. Chem. Soc.* 1868, p. 281), and made for him by A. Willis, hard steel for file-making is stated to contain but 1·2 per cent. 'Huntsman's steel for cutting tools, 1 down to 0·75 per cent.. And other examples are given with yet less carbon down to 0·18, which he designates as very mild steel. But he remarks, that 'cast-steel, containing less than 0·3 per cent is no longer capable of being hardened, and should be classed rather as homogeneous, or melted iron, than steel, while, on the other hand, an excess of carbon above 1·4 per cent again deprives the metal of the quality of taking a temper, and it must be regarded as approaching in character rather to white cast-iron.' Henry's analysis of Wootz, or Indian steel, is given in the same paper as containing 1·34 per cent.

Then as the carbon increases in amount, the various kinds of cast-iron would result. Of these the following estimates have been given:—First, Calvert and Johnson, in some experiments upon manufactured iron in its stages, give pig-iron as containing 2·275 carbon. Next, Gay Lussac, in examination of good varieties of Welsh iron, found in three specimens the quantities 2·55, 2·45, and 1·66 per cent. While, lastly, in three analyses by Brande, he found 3·22, 3·23, and 2·25 per cent. The greater the amount of carbon the more fusible the metal will always be.

Faraday and Stodart tried to 'saturate' some iron with carbon, and for this purpose they fused finely divided iron with charcoal; by which proceeding a dark grey fusible carbide of iron was obtained, so brittle that it might be pounded in a mortar; this contained 5·64 per cent carbon.

As to the formation of steel:—If an iron wire be immersed in molten cast-iron, and then allowing the metal to become solid, it be kept hot for about four or five hours, the inserted wire will be found to have been converted into steel. The conversion will be also effected if we surround the iron by charcoal, or even coal-gas (a gas very rich in carbon); or if we employ turnings of cast-iron, and, indeed, with the last agent the change will take place at a much lower temperature than with charcoal in the ordinary way. This, which is the usual method of forming steel, is called the 'cementation' process, and is effected by means of some such agent as above, which is the 'cement,' and by contact with which the outer layer of the bar operated upon, takes a portion of carbon. It has been said that this is then transferred to the next layer, while the first absorbs a fresh supply, and so on throughout the mass. But the conversion is more likely affected by means of gaseous matter. Graham, in his experiments upon the absorption or 'occlusion' of gases by metals, has found that iron at a red heat will thus take up nearly eight times its volume of carbonic oxide. Now this may part with a portion of its carbon to the metal, and again itself take carbon from the cement powder for its reconversion into carbonic oxide, and thus the steelifying action is kept up, and the supply of oxygen for the first production would be present in the air enclosed in the troughs, and porous materials of the cement powder.

Cementation is carried on in a furnace of the shape of an ordinary kiln. The lower part of this is shown in the drawing. At A, are the grate and hearth. Above this, and upon each side, is placed a long trough, B, B, often formed in fire-clay; these are about 2 feet square by 14 feet long. They are so arranged as that the fire may play under them, and its products pass away above the dome, C, by the small flue seen on each side, as also at the small square openings behind, into the main shaft or body, D. The troughs are arched or domed over from flue to flue, and at the back of the furnace a door is placed to enter for filling them.

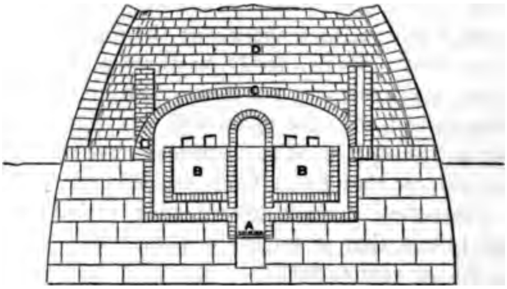

Fig. 92.

Now, in charging them, a layer of cement is first evenly spread over the bottom of each trough, to the depth of about two inches; this is a compound of ten parts charcoal with one of ashes and common salt. Upon this is laid a tier of thin iron bars for conversion; the very best kinds of malleable iron being chosen, and that variety of Swedish, known in the trade as 'Hoop L,' from its being marked with a letter L, surrounded by a ring or hoop, is much preferred. These bars are put about half an inch apart, and then between and upon them, another quantity of cement is placed. Then a second tier of bars, then again cement, and so on alternately, until the troughs are nearly full. The charge amounting to about 16 up to 18 tons of bars. Lastly, a layer of cement, then some moist sand, or a close packing of fire-clay, and upon all a luted cover of fire-tiles, so as to exclude the air.

A coal fire is now lighted in grate rising between troughs, and a full red heat got up ;—a temperature of about 2000° Fahr. = 1093° C. This is kept steadily up for about seven days.

During this time the bars gradually acquire a crystalline texture, and the progress of the operation is tested from time to time by this change of structure, a bar being withdrawn for the purpose by a hole at the end of each trough, called the proof-hole, and then broken for examination. When the operation is complete, some days are allowed for the metal to cool down gradually, after which the charge is withdrawn ; and the bars examined by fracture, so as to class them as to quality.

On examination of the product, the charge (usually of about ten tons) would be found to have increased about $\frac{1}{150}$th part in weight, and the bars externally to be covered with large blisters, from the expansion of gases within the substance ; hence the metal is called blistered steel. These blisters were supposed by the late Mr. Henry to depend upon the formation of carbon bisulphide, from the union of the sulphur (retained in small proportion even by the best iron) with carbon, the volatile gas produced raising a skin of the hot metal. Against this it may be urged that Swedish iron is smelted by charcoal, and hence contains no sulphur beyond the small traces which may have existed in the ore. Others suppose that some oxide of iron upon the metal is similarly reduced, and the effect is then due to carbonic oxide.

If the theory of the conversion depend, as above stated, upon the decomposition of carbonic oxide, carbonic anhydride as gas must be evolved from the bars, and may not this be the cause of the blistering? But all rolled metals when slowly heated have a tendency to such blistering ; thus a silver bar, or an assay ribbon of silver and gold, will often exhibit just the same surface after a slow and good annealing.

The increase of weight is, perhaps, the best test of the perfection of the steeling process, for it is not found to take place if iron of bad quality has been employed. Then, if the process be carried on too long, too much carbon will be absorbed, and the product will become so fusible that it will often run the exterior of the bars together in a mass. In fact, the metal will approach cast-iron in its character.

The blistered steel is the first, or rough manufacture, and the metal is employed in this state for files and any coarser tools; but there are several varieties of manufactured steel made for the finer kinds of cutting instruments. First of these, 'shear steel,' is so named from being employed for tailors' shears, and cutting instruments not needing great hardness. It is produced by cutting up bars of blistered steel into lengths of 2 feet 6 inches, and binding them in bundles of from five to eight or nine by a ring of steel, a rod or longer bar, being used for a handle. These are then brought to a welding heat, and welded together under a tilt-hammer. The binding ring is then removed, and, after reheating, the mass forged solid, and it is then extended into a bar. At times the bar so formed is divided and the welding is repeated, when it is called 'double-shear steel.' The product of the tilt-hammer just described is also called 'tilted steel.'

Cast steel is the best variety for the manufacture of all fine cutting tools. This is a simple mixture of scraps of different varieties of blistered steel. These are collected together for melting in a good refractory Stourbridge clay pot. In making these steel pots, as they have to stand a great heat, great care is used. The clay cannot have too much kneading, and foot treading is found to be preferable to any machine methods. A large proportion of black lead is used with the clay, and no old ground pots. They are formed in an iron mould, and the inside cavity by an iron 'former,' driven in until a given weight of clay is brought up to the top edge of the mould.*

Into each pot, previously annealed, from 70lbs. to 80lbs. of scrap steel are put, and with it a small addition of some body known to the workmen as physic. This may be some carbonaceous or nitrogenous matter with also a little flux, such as powdered glass; upon the charged pot a cover is luted, and it is then exposed to an intense heat in a wind-furnace for three or four hours; the tops of these furnaces are generally level with the floor of the casting shop, and they are fired from an underneath passage-way. When thoroughly melted, the pot is removed and its contents poured into an ingot-mould; the pot is then refilled, and so on for a third charge; after which new pots have to be employed. But the heat is more speedily got up in a warm used pot, whereby, consequently, an hour is saved in the fusion.

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* Percy gives the following materials as used for the formation of steel pots:—Edensor clay, 15 lbs.; Stannington ditto, 7 lbs.; old ground pots, 2 lbs.; ground cinders, 1 lb.

The moulds are generally long rectangular ones, and are, after heating them, placed upright for pouring into. This must be carefully done exactly down the centre, so as to fill from the bottom, for if the sides are touched by the metal in passing down, it will be cooled, and the bar turn out unsound. After pouring, a little sand is sprinkled on the top, and a small plug put in, and there is very little shrinking.

Cast steel is sometimes poured round a solid core of iron, and thus excellent compound bars are formed which, if used for purposes where they are required to be hardened, are much less liable to hardening accidents than if all of steel. The iron bar is first polished, then heated and sprinkled with borax, and then placed in the centre of the mould and the cast steel poured in.

The melting operations above described are for the purpose of rendering steel homogeneous in texture, a point of vital importance in all fine cutting instruments (surgeons' instruments, for example), for blistered steel is always slightly less carburetted as we pass to the interior of the bar; hence, when blistered is tilted, the same condition exists, although divided to just the extent to which the original bar has been cut and multiplied for welding; but in well-cast steel a perfect distribution of its elements will have taken place, but at the same time it is rendered more or less crystalline; hence the ingot from the mould must be heated in a forge and well hammered, carefully at first, until the granular particles are somewhat elongated into fibres; then the blows are increased in strength; and, lastly, the bar finished under the tilt-hammer, or by the rolling-mill. In rolling both iron and steel, but more especially the latter, great speed is used, and the work is passed through quickly while well hot, and as a red heat is used the rollers are kept cool by a stream of water.

In all kinds of steel the quality is thus much improved and especially by hammer hardening, or working under the hammer until the previously hot bar is cold; its substance will thus become much condensed. The finest kinds of cast steel for forming small tools are sold as 'Huntsman's cast steel.' So called after the originator of the process. Cast steel is now melted in very large ingots, and one of the largest yet made was that shown by Krupp at the exhibition of 1862. It was a sound ingot of 21 tons weight, and had been melted in separate crucibles containing about 70 lbs each, and poured so continuously as to form a sound casting, an example of the perfection of the organized working of a large number of men.

Referring back to the process whereby malleable iron is obtained, the excellence of which has been shown to depend much upon the absence of carbon as well as other impurities, it may strike the reader as an unnecessary proceeding, first to separate carbon to produce malleable iron, and then subsequently to add it again, for the production of steel.

This is true to some extent: hence steel is now largely made by employing the finer kinds of pig-iron, and separating the excess of carbon from it, over and above what is required to form steel. And the object is now attained by several methods. Indeed Bessemer steel is a result of attempts in this direction, but it will be presently seen that it cannot now be said to be produced without purification of the metal and subsequent addition of the requisite carbon. Before describing Bessemer's operation, some other of these methods may be briefly specified.

1st. Steel may be produced in puddling pig-iron, by arresting the operation at the point at which just the requisite quantity of carbon is left in the iron. Some manganic oxide, and sodic chloride are added during the operation. But this steel known as puddled steel, is inferior in quality, and is consequently only employed for large works.

2nd. Analogous to the last is the steel produced by Price and

Nicholson's process. They employ refined pig, and fuse it with malleable iron in the proper proportions to contain the amount of carbon needed.

3rd. Uchatius's method consists in first fusing pig-iron and granulating it. This is then mixed with oxides of iron in proper proportions, and next heated in a steel melting furnace. Thus the oxygen of the oxide takes the excess of carbon in the cast iron; carbonic oxide is formed and evolved, and the process is stopped with just the fit quantity of associated carbon.

4th. Siemens produces malleable steel direct from iron ores by melting pig-iron in a regenerative gas furnace, and then reducing the ore above the bath, allowing it to descend into, and mix with it.

He operates by first charging in about 10 cwt. of pig-iron and fusing it in the bed of his furnace (see fig. 13, p. 79) over this he places the hoppers of ore A A and passing into them a tube conveying gas. He recommends the employment of the better kinds of ores such as the hæmatites, magnetic oxides, and spathic carbonates. About 28 lbs. of charcoal is first charged into the hoppers, and then the ore.

The pig-iron is melted on the bed, and the ore in the hoppers heated in an atmosphere of reducing gas. Thus it is partially reduced to spongy metal, which is dissolved as it descends in the metallic bath below, and the reduction is completed by the excess of carbon of the metal in the bath. Fresh ore is supplied as it descends and is reduced.

The bath is tested from time to time, as to its consistence. If it is too solid, pig-iron is added to liquefy it. If it contain excess of carbon, oxidizing agents may be added in requisite proportions, and finally 5 to 8 per cent of spiegel-eisen; after which the metal is tapped out of the furnace, the great heat of which is ample to admit of the partially decarbonized metal remaining quite fluid. Mr. Siemens estimates the temperature at 2200° C. = about 4000° F.; the description of the furnace, &c. for this operation as shown at page 79 has been taken from the *Journal Chem. Soc.* Vol. xxi., p. 306, to which excellent lecture upon steel by this process, the reader is referred.

The first experiments by Bessemer were with a view to the production of iron in a malleable state without the ordinary refining and puddling operations, and in 1856 he communicated to the British Association these details of his method :—

He built a cylindrical furnace, of about 3 feet in diameter and 5 high, resembling a large crucible, and brought into the lower part, close to the bottom, five Stourbridge clay tuyeres from a powerful blowing machine. Into the vessel he ran the crude metal from the blast furnace, until it occupied about 2 feet in depth, having previously turned on the blast of air. Immediately upon running in, a violent motion was given to it by the blast, and the union of the oxygen with the carbon of the metal produced so great an increase of temperature, that not only was no heat needed for maintaining fusion, but, on the contrary, sparks and even flame issued from the top of the chamber. In about a quarter of an hour all the mechanically diffused carbon was separated, and then action arose on chemically combined carbon; this was evidenced by violent increase of action, as well as of temperature, the metal seeming to boil and becoming covered with a frothy slag; during which the other impurities, as sulphur and silicium, were stated by Bessemer to be most completely separated. Ultimately, at the expiration of some 30 to 35 minutes only, the iron was run out at a tap-hole in a pure and malleable state.

Such were the first results of the process; but it was found that much of the sulphur, as also any phosphorus was retained; and, moreover, that there was great loss of metal by its retention in the slags formed: amounting to fully 20 per cent.

But it will be readily understood that if this admirable process be applied to pig-iron, wherein these impurities do not exist, and if, also, it be stopped when the iron is brought to the degree of carbonization corresponding to that of steel, a quality of metal is produced exactly resembling good cast steel—in fact, it is the same thing—and only requires, further, the rolling and mechanical treatment necessary to develope the fibre. The difficulty, however, is to stop just at the point where the fit or a definite amount of carbon is retained. Hence Bessemer now decarbonizes as far as possible, and then assuming he has iron free from carbon, adds the latter to the desired amount, employing for this Spiegel-eisen, whose value in carbon has been first determined by analysis. This Spiegel-eisen is a hard white cast-iron, which has a silver crystalline fracture in bright mirror-like tables, whence its name. As it is reduced from spathic ores containing manganese, it always retains a considerable proportion of this latter metal, while it is at the same time very rich in carbon. 100 parts of this iron contain about 4 to 4·5 parts carbon, and an average of 10 parts of manganese, which is itself a valuable adjunct to the steel. It also retains about 1 per cent silicon, but Bessemer says that he finds ·05 per cent of silicon in molten steel valuable in destroying any tendency to ebullition, and in causing the metal to lie quietly in the mould.

The Bessemer operation is now carried on in a wrought-iron pear-shaped vessel (Figs. 93 and 94), made in two portions, and bolted together by a flange (*a*) formed upon each portion. This admits of their being lined by good fire material (*b*), over the whole of their interior. The bottom is flat for the admission of the tuyeres (*ee*) which pass through fire-brick, six or seven of which are built into the bottom, and each perforated with 5 holes,

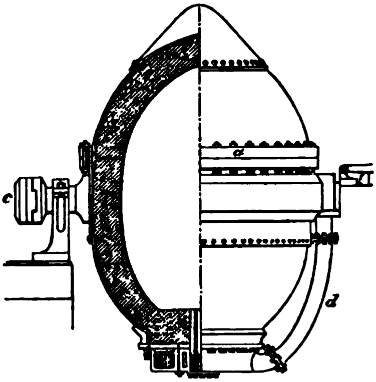

Fig. 93.

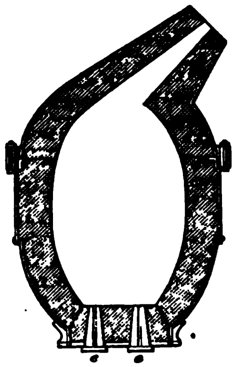

Fig. 94.

these are of about $\frac{3}{8}$ inch diameter. The top portion of the converter ends in a conical neck which opens obliquely to the side and upwards, as in Fig. 94. These vessels are made to contain charges varying from 4 to 10 tons, and are suspended on trunnions so as to be movable upon their axis (*c*), so as to turn them with the mouth either upwards or downwards, the movements being readily effected by hydraulic machinery. Through the trunnion on one side the blast is passed, and so down to the tuyeres by a pipe (*d*), carried parallel to the outside of the converter. Bessemer also employs globular converters, and in them passes the blast in at the top, carrying it down to the bottom by a fire-brick channel with openings at the lower end for the air exit.

The operation, as the author first saw it carried out at Messrs. Lloyds Fosters', at Wednesbury, was performed as follows: — A small quantity of lighted coke was first put in, and a slight blast turned on, so as to heat the vessel slightly up. This done, it was inverted, mouth downwards, so as to turn out the coke, and the apparatus was thus ready for the charge. It was next turned mouth upwards, and the blast put on, and the crude pig-iron to be operated upon was then run in by a clay-lined trough laid from the iron furnace to the mouth of the converter. The blast was first put on as described in order to prevent the tuyere-holes becoming choked by the metal.

The charge of four tons having run in, the full power of the blast (usually of about 15 lbs. to the inch) was put on; and the air thus entering the hot metal under considerable pressure, breaks up into a stream of small bubbles, which diffuse through the charge, and first attack the contained silicon, and oxidize it. This takes place without any accompanying flame. Then, after eight to ten minutes, action commences upon the carbon, and intense combustion was now manifested, and a long luminous flame of carbonic oxide, somewhat coloured by the combustion of other matters, passed out with a roaring blast, for the nitrogen of the decomposed air also rushes out, together with a shower of scoriæ, which latter are deposited in the chimney. The oxidation of portions of the iron, which also takes place, itself produces intense heat. This oxide of iron combines with silica from the oxidized silicon, and thus a slag is formed which is constantly thrown up to the mouth of the converter. After some eighteen minutes the flame at the mouth appeared paler, for the metal had then parted with nearly all the carbon; and the operation was carried on until sparks of pure iron in combustion were showered out of the converter. The operation was then stopped, as the vessel contained only pure malleable iron, and kept quite fluid by means of the intense heat developed by the active chemical action which had been carried on. Lastly, the proper quantity of Spiegel-eisen was added, or just the amount required to carbonize the iron to the extent of producing steel. After this addition the blast was again turned on gently, so as thoroughly to mix the metals. This done, the whole was cast in iron ingot-moulds.

For casting, the metal is run into a large ladle lined with fire-loam, and of a size to contain the converter charge. It is furnished with an opening at the bottom, closed by a plug, so as to allow of the contents being run in successive quantities into moulds.

Considering that from 5 to 10 per cent of Spiegel-eisen is added, it will be evident that a large quantity of manganese is thereby introduced into the steel; and it is found that traces of other metals, or even more considerable quantities, in some cases, improve the quality of steel. Thus Faraday and Stodart proposed adding small quantities of rhodium, silver, or chromium, either of which is said to improve the product. Mushet patented a process for adding titaniferous iron to steel: and of late an iron-sand has been found in abundance in New Zealand and other places, which contains about 12 per cent of oxide of titanium associated with magnetic oxide of iron. Portions of this have been reduced in England, and manufactured into steel, under the name of 'Taranaki steel,' from the place where the ore is found. This has been found to work most admirably into the finer kinds of cutting instruments, the polish and edge of which are superior to those attained in ordinary kinds of steel, but whether due to the titanium or not is a question. Riley says he has failed to detect the virtues of titanium in iron; tungsten, in steel, adds much to its value for magnetic purposes. But the true value of all these alloys is yet a very open question.

The delicacy of the observations made by the spectrum apparatus has brought it into use for examining the Bessemer flame, and by it the point at which the carbon is all oxidized and burnt off may be very accurately determined. Silliman, and also Parker and others, have examined the flame by the spectroscope, and also by various coloured glasses, and some curious results have thus been obtained.

A process has been produced by Mr. Heaton for the production of steel, similarly by oxidation of the carbon and silicon in pig-iron; but, in place of using atmospheric air, he employs sodic nitrate as an oxidizer.

A quantity of this salt is introduced into a chamber formed at the bottom of a fitting converting vessel; upon this the melted metal is run, and, at once decomposing, the soda-salt sets its oxygen free, which acts most energetically upon the carbon and silicon of the metal, so that purification is said to be complete in about five minutes. The metal is then removed in a pasty state, and treated for the removal or separation of the slag formed.

For shaping steel into the various forms required in cutting and other instruments, it is necessary that it should be quite soft; but, after forging, it requires hardening sufficiently for its uses; and although hammer-hardening condenses the grain and improves its texture, as it does in most other metals, yet, in order to get perfect and uniform hardness, other plans have to be pursued, whereby perfect hardness is ensured; and then, for use in the various kinds of cutting-tools, &c., this hardened state is again lowered down to a fit degree by a subsequent operation called tempering, or 'letting down.'

Now the hardening operation is based upon the fact that when steel is heated up considerably and then suddenly cooled down, it acquires an extremely hard condition; and the wider we can separate the two points of hot and cold, the more perfectly hard it will become. The practice, therefore, is, first to heat up the metal to a full red heat, and then suddenly plunge it into cold water or some other similar medium; and that the effect is the result of this difference is proved by the fact that, if we are unable to cool to any very low temperature, we may use such as can be controlled; but in that case the heating up must be to a higher temperature in proportion, or the metal will remain soft. Where great extremes of temperature are used, the metal may be rendered so hard as to be quite unfit for any practical uses. This property of so becoming hard is one of the distinguishing points between malleable iron and steel, for the former will not become sensibly harder or brittle by such treatment.

But the great difficulty in hardening steel depends upon the circumstance of its being subject to the same accidents as glass, although, of course, in somewhat less degree; for, like imperfectly annealed glass, hard steel will crack and fracture, or even fly to pieces by blows or sudden changes of temperature; or, another evil is the distortion which may take place during hardening, and this may occur to the extent of rendering otherwise finished work quite unfit for the purposes for which it has been prepared. Such casualties will be readily accounted for, when the manipulation and principle of the hardening processes have been explained.

In heating up the work, our main object is to render all parts requiring to be hard of a uniform temperature; hence large works are placed either in a forge or else in a box or pan of charcoal; and they may be protected in a crucible or convenient case of crucible ware, or even heated in a muffle where such a chamber is available. If the heating be in the open fire, it is best to employ cinders or coke as a fuel (charcoal is the best fuel), and to get the heat up as well as possible before introducing the work; for if much bellows be used afterwards, the surface is apt to oxidize. Hence the work is put into the hot fire, and well 'soaked,' as expressed by the workmen. It is then turned about so as to expose all portions equally to the heat; and it is safer to be under than over the mark in heating, for over-heating is sure to oxidize the work. And, again, it is always found that steel which is attempted to be hardened after being too strongly heated is really rendered by no means hard; and, moreover, the texture seems to be altered, for its tenacity is destroyed, and it exhibits a very coarse-grained fracture, and it may even bring it into the condition of 'burnt steel,' in some cases. On the other hand, less than the required degree of heat in place of hardening, will even soften the metal, notwithstanding its plunge into the cooling medium; at any rate it tempers it, and indeed will equalize its natural hardness.

A consideration of the degrees of heat which are required in the after-process of tempering, or adapting the work to its particular use by lowering its hardness, and consequent brittleness, may give us some clue to the amount of heat required in the operation we are considering. This degree ranges from 420° to 650° F. = 215·5° to 329° C.; and it may be stated that as we cannot harden up to any desired point, as might be supposed, we are obliged in all cases (as before remarked), to harden well up, and then lower down to such needed degree. Hence, to harden effectively, the heat used must be somewhat above the highest of these degrees, and, indeed, very considerably above when extreme hardness is needed; or, if this cannot be effected, we must, on the other hand, cool correspondingly low.

Besides the plans for heating up already mentioned, smaller work, especially if there be many pieces and they require a tolerably uniform hardness, may be heated in a bath of melted metal, heated mercury, fusible metal, or, better and more practical than all, a bath of fused lead. Thus an uniform temperature of about 617° F. = 325° C. is ensured. Of course, the heating up of very small work is yet much easier; such may be heated even in a candle or lamp flame; and, if need be, the temperature of the latter may be increased by means of the blowpipe. They may also be readily heated by placing them between the jaws of a pair of hot tongs.

The use of some carbonaceous material, surrounding the heating metal, will at once be recognized, when the nature of steel is remembered, for by it the surface of the metal is kept from alteration during heating. And for this purpose a salt-like potassic ferrocyanide is similarly used, being sprinkled on the surface, after a preliminary gentle heating, sufficient to fuse it over, and varnish the metal surface.

Passing now to the cooling operation, it may be observed that, as a medium for effecting it, cold water is to be preferred to all others, although we are somewhat controlled as to its use by the size of the work operated upon; for in the case of very small and delicate instruments, it would render them too hard and brittle. Hence, for such, it is a common practice to heat them up with a candle, increasing its power, if needful, by the use of a blowpipe, and, when of sufficiently high temperature, very suddenly withdrawing from the heat, and plunging them into the substance of the candle, when the required coldness is afforded by the cool tallow.

Secondly. Small but somewhat larger objects than the last, after being similarly heated, may be cooled by being placed upon a solid mass of cold metal, which by its conducting power will rapidly withdraw the heat; but it is always advisable to cover at the same time with a corresponding cold piece, or the side touching the metal will be harder than the upper one, and by consequence the work will be distorted just in the same proportion.

Thirdly. As the work increases in size, more direct means may be used, and thus cold oil is at times employed; while, lastly, we come to the use of water, and here, where the mass of metal is large, it is even customary to cool down to about 40° F. = 4·4° C, especially where the quantity of water would be small in comparison to the bulk of metal so as to be quickly heated up by it.

Some operators state that the hardening water should never be quite cold. Mr. Ede says that the chill should be taken off, and the water raised to about 60° F. = 15°·5 C. On the other hand, the late Mr. Brande, whose experience in the delicate hardening of coinage dies was very great, says that the hardness got in warm water never equals that of cold; he says that a red heat and water at 45° F. = 7°·2 C. is the most desirable for die hardening. In Mr. Freemantle's Mint Report for 1870, he states the durability of the dies to have been much improved by very gradually heating them before plunging in cold water.

Mercury has been recommended in place of water for hardening, as in itself a good conductor of heat, and also because it is said that on the first immersion of a piece of hot metal in water, the particles adjacent are converted into steam, and by this the metal is to some extent protected from the influence of the cold. But against this objection it may be stated that the formation of steam cannot be effected without the abstraction of much heat, for 970° F. must be taken into the latent state by the water before its physical condition can be so changed. And again, mercury is very readily vapourised, and the metal is thus equally surrounded by vapour. Nevertheless when extreme hardness is wanted, mercury is effectively used. But its weight, bulk, and cost, render it only applicable to small work.

Oil is largely used as a hardening fluid, and is said to render the metal more tough, while it hardens it well for its uses. The oil is used in general cold, but sometimes heated up somewhat.

The execution of this cooling operation is a matter requiring extreme care. For example, if the work be a long and comparatively slender instrument, it must be plunged perfectly vertically, and as quickly as possible; for, suppose it to be carelessly thrust in sideways, or at any considerable angle to the surface, the part first touching the cooling medium will be contracted, and the instrument bent, and irrecoverably so, notwithstanding the other parts being in turn subjected to the cooling influence; because, metals being such perfect conductors of heat, the action of the water does not take place upon the upper surface at near so high a temperature as it did upon the under, for conduction will have acted as much as the rapidity of the operation will have allowed of, and certainly sufficiently so to upset the balance of so delicate an operation, and so to render the tool unequally hard and considerably distorted.

In immersing larger and more solid works, if of unequal form in the various parts, any portion containing the greatest bulk of metal should be plunged in first, and here again the same principle operates, not only producing distortion, but also that unequal condition of particles, which renders hard steel so analogous to glass; for, in such large masses, the first effect of the cold is to harden a crust externally; this contracts upon the inner particles, and keeps them in a considerable state of tension; and these internal ones cannot be brought into the same hard and contracted state as the outer, for the abstraction of heat from the latter will by just the amount elevate the temperature of the cooling material, and so weaken its efficiency. Hence so constrained a state of particles is produced that they will be exceedingly liable to restore their own balance by spontaneous cracking or fracture, which may take place during the cooling operation, or, at any rate, upon the action of the least external force subsequently—as a blow or fall, for example. This spontaneous rupture of a piece of hard steel, if of any size, is often attended by a very audible crack or report.

In general, the application of cold contracts bodies, diminishing their bulk and increasing their specific gravity, but the opposite is true of the effect of cold in hardening steel. This fact has been long known. Thompson (writing in 1831, in his *Inorganic Chemistry*, vol. i. p. 497) states that he found some good blistered steel having a gravity of 7·823, was lowered to 7·747 by hardening, and some cast steel which in the soft state had a specific gravity of 7·8227, was reduced to 7·7532. He says, 'Doubtless the volume which it acquired on heating it to redness is retained, the cold water solidifying the surface before the mass has time to contract.' Reaumur gives the increase of volume as $\frac{1}{48}$th of the whole mass. If hardened steel be slowly annealed it will recover the original gravity which it had in the soft state. Percy corroborates these facts, and states that Rinman found two pieces of steel whose gravities before hardening were 7·751 and 7·991 respectively, had them decreased to 7·553 and 7·708 by hardening them.

In simple hammer-hardening, the reverse is, of course, the condition, viz., condensation and consequent increase of specific gravity. Thus a specimen which had a specific gravity of 7·833 by hammering rose to 7·872; and these again, when hardened in the usual way, were diminished, the first to 7·816, and the second to 7·818. (Brisson.)

In conclusion, it must be stated that all complex steel instruments should be forged and wrought previously to hardening, with as much freedom and regularity of substance as they will admit of; otherwise parts which have had most hammering will be more dense than the others, and their particles will be, to some extent, in this state of constraint, even before they are called upon to sustain the extreme tax they have to bear in hardening. And it may be remarked that steel is more difficult to forge than iron, and consequently requires more care.

As this capability of hardening occurs in steel and not in iron, it may of course be assumed to depend upon the presence of carbon in the latter, and hence cast-iron is found from this cause to admit of hardening, and thus, what are known as 'chilled castings' are simply cast-iron work which have been produced in a mould of metal, which by its good conduction has rapidly cooled down the surface of the molten metal, and rendered it superficially hard in consequence. But it is a curious fact that this action is most effectively carried out by pouring the metal into a mould somewhat heated up, rather than into one which is perfectly cold.

What is termed 'case-hardening' is really the formation of a casing of hard steel upon the surface of an iron article, and the operation consists in simply smearing the surface of the iron with some body rich in carbon, and capable of ready decomposition at a high temperature; and then heating up considerably. There are many methods of carrying this out, but the following is the best. The surface of the work is first finished as carefully as possible, after which it is heated up to bright redness. It is then sprinkled over with potassic ferrocyanide (or prussiate of potass). Now this is a salt which contains iron in itself, together with cyanogen (a gas rich in carbon), combined with potassium. It is decomposed at the high temperature of the iron upon which it is sprinkled, and its carbon is at the same time united with the surface metal, and converts it into steel. The work is next heated to full redness, and plunged into water, as in the ordinary hardening operation. Sometimes in place of the above method of using the salt, it is made into a thin paste by mixing it with clay, then the metallic surface is coated with this, heated, and hardened.

Mr. Roberts, in speaking of this operation (and it is one often performed in large engineering works), says, that 'where the heat is managed well, so as not to overheat the work, but is gradually got up over a space of 4 or 5 hours, the steelifying action may be made to penetrate some $\frac{3}{8}$ths of an inch.' But in general it penetrates about $\frac{1}{16}$th of an inch, as in gun-locks and the like.

In large engineering works it is customary to employ in the place of the salt mentioned, horns, bones, or leather cuttings, to heat the metal with. In fact, any body rich in carbon, and easily decomposed; but the agents found most effective are those which, like the ores mentioned, contain hydrogen also. Indeed pure carbon, as wood charcoal, will not serve this purpose.

In some few cases the hardening operation is the final one, but in the majority, as for cutting-tools, drills, springs, and in many other applications, the hardened work needs tempering or letting down; and as certain tints or colours produced upon the surface of steel are serviceable as indications of its state of hardness, so these are always taken advantage of in effecting the tempering operation. Passing up through these colours, commencing with those shown in softer states, they will be in the following order. First, pale blue, passing to green, is an indication of great softness, such as would render any instrument quite unfit for cutting purposes, this tint is arrived at by reheating hard steel to a degree between 580° and 650° F. = 304·5° and 343° C.

Next the darker shades of blue, up to purple, as seen upon clock and watch springs, indicate a degree more hardness, but with just sufficient of the opposite property to diminish their brittleness. These tints appear at 550° to 570° F. = 288° to 299° C.

Then a brown yellow, shading off to purple, is produced by heating from 500° to 530° F. = 260° to 276°·5 C. This is employed for instruments which have to resist blows, or jars, as in the case of saws, where the teeth actually strike upon the material each time the cut is reversed, or hatchets, adzes, and the like.

Lastly, the various shades of yellow, from very pale to dark straw, arise at degrees between 420° to 500° F. = 215·5° to 260° C. The darker straws are preferred for wood tools, screw-cutting apparatus, and the like, and the paler for general metal tools.

After having formed and hardened the instrument, the first step in tempering consists in cleaning the surface free from scale, and then polishing a portion. If it be a small article, it is next carefully heated in a candle or lamp, the bright part being closely watched, and immediately the required colour is produced, the work is to be quickly removed and plunged into cold water as in hardening. In truth, this process resolves itself into a kind of hardening operation, the previous one being but a preliminary step, whereby the operator ensures his having hardness sufficient, which is brought down again to the required degree by this second one. This is, indeed, proved by the fact that if the metal be allowed to cool slowly, after heating to colour, it would by so doing undergo a kind of annealing, and become again converted into soft steel. But the quick cooling determines its hardness, corresponding to the tint down to which it has been softened.

A very good method of heating small works for tempering is effected by heating a bar of iron well red at one end, and then fixing it in a vice, thus progressing to the cold end, any required temperature may be ensured, and the temperatures of different parts of the heating bar will be soon learned by experience, presuming that one of the same size is always used, and it be heated uniformly.

Some mechanics use a method of forming and hardening small works without tempering, by employing a manipulation based upon the fact, that a long instrument after hardening will exhibit gradations throughout its length from extreme hardness at the point which first touched the cooling medium, down to comparative softness at the further end. Hence they take a piece of steel much longer than needed, and harden it. It is next ground away until a part is arrived at where its temper suits the object required, at which point the tool is fashioned. But this plan, requiring much experience, is not always successful.

A very convenient and practical method of tempering, especially where many articles have to be done at the same temperature, is carried out by heating them in a bath of some kind, whose temperature is regulated by immersing a thermometer in it. Thus oil is very often employed in this way, and similarly metallic baths may be used.

Large masses of steel will be hardened by heating and simply cooling in the air, which is sufficiently effective at its ordinary temperature. Thus large steel castings become very hard on the surface, unless means are taken to prevent this hardening action of the air.

Annealing is only effected in steel by heating, and then slowly cooling out of air contact. Large works are therefore heated, and buried in dry sand, or lime. Others in sawdust, smaller, are commonly heated up in a box of charcoal powder, and allowed to cool very slowly while thus protected. There are many cases where during the fabrication of a piece of work in which hardening takes place, that annealing must be resorted to; for example, in forming a die, the punch employed soon hardens the surface of the soft die, and that before a sharp impression can be got; it must, therefore, be annealed as above, indeed several times over before completion, after which it is finally hardened in the usual way.

It is often needful to weld iron to steel, and indeed many cutting instruments are formed of this compound metal, as, for example, axes, plane irons, and tools where the hardness of steel is needed to be joined with the toughness and tenacity of iron. The difficulty arises in the difference of the softening and fusing points, but this is got over by heating the more fusible steel to a lower degree than the iron, or by the method already mentioned of cleaning and heating the iron to redness, and then, after cleansing its surface with a little borax, pouring the fused steel upon it when union takes place, which may be completed by hammering.

In conclusion, it has been already stated that the capability of being hardened by sudden cooling affords a means of discriminating between steel and iron; and another ready means consists in dropping a little nitric acid upon the metal. If it be a piece of iron, solution will take place, and a green spot appear from the iron salt formed; but if it be steel, the spot will be grey, dependent upon the carbon set free during the solution of the metal containing it. Again, steel will ring when struck and its surface oxidizes much less easily than iron. The texture of malleable iron is ether crystalline or fibrous. The former the natural condition, the latter the result of mechanical treatment, where the crystals are elongated into fibres. But the fibrous condition may revert to the crystalline under the influence of a succession of vibrations or blows. Percy says all iron after heating sufficiently to induce pastiness is sure to become crystalline; then cold hammering or vibration or continued jars may induce fracture at crystalline faces. He further states that if iron is melted which is largely crystalline, and then forged for rolling and rolled into bars, they will present a crystalline or fibrous fracture according to the method of breaking, and time occupied in doing it. Thus if nicked on each side, and bent backwards and forwards, the fracture will be highly fibrous; but if nicked all round and then suddenly broken, the fracture will be crystalline.

Good cast-steel has a fine granular fracture on breaking, and this may be rendered finer by hammering. In the best kinds it will have a silky appearance, and somewhat of silvery whiteness. In steel, again, the fibrous structure is an artificial one, the result of fagotting and rolling, and most useful for many of its applications, as, for example, the formation of springs and the like. But such would be unfit for cutting tools, and for these the fine-grained steel such as is produced in the best kinds of cast-steel, as already described, is a necessity.

Chemically pure iron is not easy of preparation, although many methods are described for effecting it. Percy says the only pure iron he has seen was made by electrolysis and from a mixed solution of the chlorides of iron and ammonium. It has been recommended to prepare it by heating precipitated ferric oxide in a current of hydrogen; but as this plan necessitates the employment of pure material, and as the pulverulent metal obtained is very liable to spontaneous oxidation in the air, the following method of Berzelius is the one usually adopted:—

Clean ordinary filings are taken and mixed with about one-fifth their weight of fine ferric oxide. The mixture is put into a refractory crucible, and covered with a layer of green bottle glass; such being used, as it is free from plumbic oxide. The whole is luted up and heated for an hour to whiteness. In this way, traces of carbon and silicon are oxidized by the oxygen of the iron scale, and such foreign matters removed by the glass flux, when a button of pure iron subsides in the pot.

Properties.—Pure iron is grey in colour, and its surface admits of an extremely high polish, increasing with its hardness. This polishing, to some extent, diminishes its tendency to oxidation, which takes place very readily in ordinary, when air and moisture are present; and when once oxidation has commenced, it goes on very rapidly to destroy the metallic surface. As a proof that the air is the agent in this, it may be stated that iron may be immersed in water without change, if care has been used to free the latter from air. Oxidation may also be prevented by contact with any metal which is more electro-positive; thus any delicate steel instrument may be protected from rust by wrapping it in very thin sheet zinc; and in this way articles of fine cutlery are at times sent by sea, and so perfectly protected from rust.

Iron burns readily at a high temperature, and its combustion in oxygen gas is very vivid when a red-hot wire is introduced into a jar of it.

It is soluble in nitric acid, also in dilute sulphuric, or in hydrochloric acid. Strong sulphuric has little action upon it, even if boiled in it. It is readily attacked by chlorine, iodine, or bromine. It possesses the peculiar property of becoming 'passive' or unacted upon by certain acids under some circumstances.

Thus a piece may be kept for some months in strong nitric acid without action. This may be brought about, by touching it under the acid with a platinum wire, or by oxidizing the end of an iron wire by heat, before immersion. Various explanations are offered, but for a description of the condition, &c., the reader is referred to Miller's *Chemistry*, 4th edition, vol. ii. p. 580.

The specific gravity of iron is 7·844; and referring to the table, page 15, it will be seen to stand first in tenacity, fourth in ductility, and sixth in malleability, as compared with the metals there mentioned. This latter character being much impaired by the presence of impurities. Specific heat, 0·113795.

It is one of the magnetic metals, but its magnetism is destroyed by heating to redness. At a strong red heat it will become quite soft and pasty, and two cleansed surfaces will then hammer together, becoming perfectly homogeneous or welded. Metals generally pass at once to fusion, but iron retains the pasty condition through several degrees of heat. The practice of welding is to heat up the pieces to be united, and by sprinkling them with a flux, such as sand, or silica, any oxide formed is dissolved, and the fluid silicate flowing over, protects the hot metal; on hammering, this slag is driven out, and contact of the metallic particles in the soft state is brought about; in fact, as close a union as exists between the particles composing the separate pieces of metal. Heated above the welding point which Siemens estimates at 1600° C. = 2900° F. it breaks up and fuses.

For its actual fusion the strongest heat obtainable in a wind-furnace must be employed. Iron containing carbon, either as steel or pig-iron, is much more fusible and expands so much on cooling, that exceedingly sharp castings are got from it; hence the beauty of detail in much of the cast-iron in daily use. This is especially shown in the fine Berlin ornamental castings. Its symbol is Fe''. Fe'' Atomic weight, 56.

Compounds of Iron.—*Oxides.*—Four may be enumerated:—1st. The protoxide, or ferrous oxide, the base of the green ferrous salts, composed of 1 atom of iron with 1 of oxygen. 2d. Sesquioxide, or ferric oxide, also a salifiable base, where 2 of iron are in union with 3 of oxygen. Ferric oxide forms with acids the red or ferric salts. 3rd. A black oxide known as magnetic oxide, composed of 1 proportional of each of the two first, and hence being a compound of 3 of iron with 4 of oxygen; the ordinary scale of heated iron is this oxide: it constitutes the loadstone, or natural magnet, and also an abundant ore from which Swedish, American, and some other irons are obtained. 4th. Ferric acid, obtained only in combination with alkalis, to which it plays the part of a weak and unstable acid. Thus, if ferric oxide be further oxidized by heating with potassic nitrate, the higher oxide produced combines with potassa, forming potassic ferrate.

The first compound, or ferrous oxide, may be obtained by dissolving a ferrous salt in water, as free as possible from air, and then precipitating by an alkali. Thus a white hydrate falls, which rapidly passes to green, and ultimately to reddish brown, by absorption of oxygen. If air be as much as possible got rid of during its preparation, and the precipitate be boiled cautiously, it becomes black from loss of its water of hydration. It cannot be isolated from the fluid, for any attempt to dry it ends in its conversion into ferric oxide. Symbol, $Fe\,O$. Atomic weight, 72.

Ferric oxide is obtained in a hydrated state by dissolving iron in nitro-hydrochloric acid, and adding to this solution ammonia in excess: in this way, a bulky brown hydrate falls. This is so gelatinous as to be very retentive of the precipitant, and thus requires careful long washing. It may be dried at 212° F. (= 100° C.) without losing its water, or rather, retaining 1 proportional; to drive off this, a temperature of about 600° F. (= 317° C.) is required. The hydrated oxide readily dissolves in acids, and forms salts; but when thus deprived of its water, it becomes very insoluble in acids. The ordinary rust of iron is composed of this oxide, as are also some of the ores of iron — brown hæmatite, for example. It is prepared for use in the arts and manufactures, by decomposing ferrous sulphate by ignition, and according to its state of division is sold as colcothar, crocus, rouge, &c. In these forms it is employed in the ceramic arts for red, brown, or violet colours, dependent on association and treatment; also as a polishing powder in plate-glass works, and as rouge for a silversmith's polish. Symbol, $F'''_2\,O_3$. Atomic weight, 160.

The black or magnetic oxide may be prepared in the hydrated state from a solution of ferrous sulphate, made fresh and treated as follows:— two-thirds of the quantity is taken, acidulated with sulphuric acid, and then boiled: nitric acid is then added to convert the ferrous into a ferric salt. The effecting of this is shown when no more nitric oxide is given off on adding the acid. The solution is then mixed with the one-third remaining of the original ferrous sulphate, and the whole precipitated by ammonia and boiled, thus a black crystalline oxide goes down of the formula $Fe_3\,O_4,\,H_2\,O$.

Chlorides.—There are two, corresponding to the oxides just described: The first, or ferrous chloride, may be obtained by dissolving iron in hydrochloric acid, and crystallizing; thus green crystals are obtained, composed of $Fe\,Cl_2 + 4\,H_2\,O$. It may be obtained in the anhydrous condition by igniting iron in a tube and passing dry hydrochloric acid gas over it. Thus white anhydrous ferrous chloride sublimes.

Ferric chloride may be obtained by dissolving ferric oxide in hydrochloric acid, and evaporating the solution: thus deep-red crystals are obtained, composed of $Fe_2\,Cl_6 + 6\,H_2\,O$. The anhydrous ferric chloride is formed by passing dry chlorine over iron heated to redness when this compound sublimes in deliquescent brown scales.

Sulphides.—No less than five have been enumerated, but of these only two are important: first, a protosulphide may be precipitated as a black hydrate by adding an alkaline sulphide to a ferrous salt; but if allowed to remain a short time in the liquid, the iron will be sesquioxidized, and its sulphur set free. Ferrous sulphide may be obtained (but mixed with more or less sulphur or iron, as either may have been in excess) by heating a mixture of iron-filings and sulphur together. In this way we get a metallic-looking mass, which is our source of dihydric sulphide. The composition of this sulphide is Fe S. Atomic weight, 88.

The interest of the bisulphide or ferric disulphide consists in its large diffusion as iron pyrites. It is found generally crystalline, in cubes or prismatic forms, having much metallic lustre and a specific gravity of about 5·0. A variety, not generally crystalline, occurs largely in nature as magnetic pyrites. Iron pyrites, from its containing 53 per cent of sulphur, is used as a source of sulphur in the manufacture of sulphuric acid; but, as it commonly contains traces of arsenic, such acid is very liable to be contaminated with the latter. It is also a large source of the copperas of commerce, or impure ferrous sulphate. Composition, $Fe\,S_2$. Atomic weight, 120.

Ferrous Sulphate.—This salt may be obtained in a pure state by dissolving iron in dilute sulphuric acid, filtering as much as possible out of contact with air, and crystallizing; but it is an article of large commercial use under the name of copperas,—a corruption of the French *cuperose*, so called from the brownish-red colour the crystals assume from absorption of oxygen in moist air, and, as such, is prepared from alum schists, which contain much disseminated iron pyrites in fine division. In the calcination of these alum ores for the formation of aluminic sulphate oxidation of the pyrites occurs at the same time, and with ultimate production of ferrous sulphate. The calcined material is lixiviated, and thus the two sulphates are obtained in mixed solution, and are separated by crystallization; for on evaporating, the ferrous sulphate being the less soluble of the two, crystallizes out, leaving the more soluble aluminic sulphate in solution. The salt so obtained is, however, very impure; it often contains as much as 2½ per cent of alum, and always a quantity of ferric sulphate, whence it has a dark apple-green colour. The pure salt is of a blue green. The composition of the crystallized salt is $Fe\,S\,O_4 + 7\,H_2\,O$.

Ferric sulphate may be obtained by dissolving one proportional of ferrous sulphate in water, and adding half a proportional of sulphuric acid. The mixture is boiled and nitric acid gradually added, until nitrous fumes are no longer produced. The solution is then evaporated to dryness, so as to expel the remaining nitric acid, when the ferric sulphate remains as a white and somewhat insoluble salt. Composition, $Fe'''_2\ 3\,S\,O_4$.

Ferrous carbonate is of interest as forming a most important ore of iron, our clay and black band ores being, as already stated, impure carbonates.

In the laboratory we obtain ferrous carbonate by adding an alkaline carbonate to a solution of a ferrous salt. It then falls as a bulky green hydrate, very unstable, as it is readily oxidized by exposure to air. It loses its carbonic acid at the same time, becoming converted into hydrated ferric oxide. Composition, $Fe\ Co_3$.

The artificial alloys of iron with other metals are none of them of any practical importance. In plating iron with zinc or tin partial surface alloying of the former takes place. Alloys of iron, with tungsten, titanium, chromium, arsenic, and at times with manganese, are found in nature. It alloys also with the noble metals.

In the discrimination of iron, the characters brought out are very distinctive, and much varied according as the metal may be in the state of protoxide or of sesquioxide in the body under examination; but the great tendency of the former or ferrous compounds to absorb oxygen causes them always to give more or less indication from the application of tests properly belonging to ferric salts.

An iron compound of either degree of oxidation will, when heated in the blowpipe-oxidizing flame with a little borax, give an orange-yellow bead. If this be removed and heated in the reducing flame, it is changed to green, the iron being so reduced to protoxide.

1. *Reactions of ferrous salts.*—The solutions will be of a green colour, and no precipitate will be produced by dihydric sulphide in an acid solution, but there may be a slight one if the solution be neutral.

2. Ammonio-hydric sulphide will produce a black precipitate of ferrous sulphide, which is insoluble in excess of the precipitant.

3. The alkalis, potash, soda, or ammonia, produce corresponding precipitates of hydrated ferrous oxide. This, at the moment of its formation, is white, but passes rapidly through

shades of light green, dark green, and ultimately brown—the latter being an indication of its conversion by air into ferric oxide. If ammonic chloride be present in the solution when the ammonia test is added, it will re-dissolve the ferrous oxide thrown down.

4th. The characteristic test is potassic ferridcyanide, which produces a deep blue precipitate, known as Turnbull's blue. On the other hand, when this test is applied to a solution in which the iron exists as a ferric oxide, it merely changes the colour of the solution to a dark green, without forming a precipitate.

Reactions of ferric oxide.—1st. Dihydric sulphide produces a white precipitate of sulphur, which renders the solution milky: this depends upon the reduction of the ferric into ferrous oxide, by its oxygen uniting with hydrogen of the dihydric sulphide, and forming water.

2nd. Ammonio-hydric sulphide throws down ferric sulphide, which in colour and appearance resembles the ferrous sulphide.

3rd. Alkalis throw down a very bulky brown hydrate. This is not soluble in excess of the precipitant, and, when produced by ammonia, the precipitation is not affected by the presence of an ammoniacal salt.

4th. Potassic ferrocyanide may be named as a characteristic test: it produces a precipitate of Prussian blue. This test does not so act in ferrous salts, but, with them, gives a white precipitate, which, however, becomes blue by exposure to air, and consequent oxidation. Potassic ferricyanide gives no precipitate, but merely a green colouring.

5th. A solution of potassic sulphocyanide gives a blood-red colour to a solution of a ferric salt. And this reaction is not only very characteristic, but takes place in very dilute solutions.

6th. Tincture of galls will immediately blacken water containing very small traces of ferric oxide in solution. Ordinary writing-ink is thus formed.

Iron is always estimated as peroxide or ferric oxide, and for this purpose a solution containing it is always boiled with a little nitric acid, or with potassic chlorate, or some other oxidizing agent. After this the oxide may be precipitated by excess of ammonia, washed, dried, ignited, and weighed, and every 70 per cent of this ignited precipitate will be iron.

The presence of citric or tartaric acid, as also many analogous organic bodies, will much hinder precipitation by ammonia. In such cases it is better to precipitate by ammonio-hydric sulphide, and then, after redissolving this precipitated sulphide in nitric acid, to throw down ferric oxide in the usual way by means of ammonia.

Iron may be separated from most of the metals hitherto considered, by virtue of its non-precipitation, by dihydric sulphide. Thus, to give an instance, the analysis of copper pyrites (a mixed sulphide of iron and copper) may be briefly detailed.

The mineral may be boiled with strong nitric acid; this dissolves the iron and copper, and separates the sulphur. The oxidizing influence of the acid may convert small portions of the latter into sulphuric acid; and it also peroxidizes the iron. The sulphur then being filtered away, the copper is precipitated by dihydric sulphide, the precipitate is filtered out, thoroughly washed, and partially dried, so as to be able to separate it readily from the filter; this is done, throwing the precipitate into a beaker, and adding the ash of the filter, which is subsequently burned for the purpose. The whole is then treated with nitro-hydrochloric acid, by which it is oxidized, and its sulphur separated; after which the copper is precipitated as oxide by potass, boiled, filtered, washed, ignited, and weighed. (See page 382.)

Lastly. The iron solution, filtered away from the precipitate formed by dihydric sulphide, is to be again boiled with a little potassic chlorate, lest any of the iron may have been reduced to the state of ferrous oxide by the dihydric sulphide; after which it is to be precipitated by ammonia, and separated as above described.

The separation of iron from alumina has already been spoken of, and it may be further stated that in place of the method described (page 416), they may be precipitated by potash instead of ammonia. The liquid should have the precipitate digested in it for some time, in order that the potash may dissolve out the alumina, and after filtration the iron precipitate is to be well washed before drying and weighing.

From magnesia, ammonia will separate iron (as it will also from alkalis), but some magnesia, is sure to go down with the iron unless the operator is careful to add a considerable quantity of ammonic chloride before precipitating by ammonia.

CHAPTER XVIII.

MANGANESE AND COBALT.

The two metals now to be briefly examined are not employed in the reguline state, and of their compounds, their oxides are the ones most largely useful.

The common ore of the first is the source whence large quantities of oxygen are obtained by the chemist, and it is also used as a secondary body in the production of chlorine. Again as a flux and a colouring material for glass. Then the metal itself enters in small quantity as an alloy into some forms of iron and of steel, for few iron ores are free from manganese, which becoming reduced with the iron alloys the latter; then as the Bessemer steel process is now worked, and the purified iron is recarbonized by Spiegel-eisen, as has been described; a quantity of manganese is by this addition added to the steel.

Compounds of the second metal, cobalt, are used in forming several brilliant pigments, and also as colouring fluxes.

MANGANESE.

The principal ore of this metal is the native dioxide. The minerals Wad and Psilomelane are amorphous varieties. The crystalline forms are the hydrated oxides Pyrolusite and Varvicite.

Metallic manganese may be prepared from the common native black oxide, by first treating it with hydrochloric acid. This converts the manganese, and iron also, which is associated with it, into chlorides. These are dissolved out of the mass, the solution evaporated to dryness, and then heated so as to volatilise ferric-chloride. The residue is then digested in water, filtered, and precipitated by sodic carbonate; pure manganous carbonate falls, which on heating leaves a pure oxide. This latter is to be heated intensely in a charcoal lined crucible, when it will be reduced, but the metal will retain a little carbon, which latter may be removed by again fusing with borax. Thus a greyish white metal is obtained, of a granular texture, but so greedy of oxygen that it can only be preserved in sealed tubes, or, like potassium, under naphtha. The specific gravity is 8·013. Symbol, Mn. Atomic weight, 55.

There are no less than six oxides of manganese. The first, manganous oxide, or protoxide, forming the basis of all ordinary salts of the metal. If potassa be added to a manganese salt, we get this oxide precipitated as a bulky white hydrate, which soon becomes brown by absorption of oxygen. The anhydrous protoxide is a green compound, and may be obtained by heating manganic dioxide in a current of hydrogen gas. Protoxide or manganous oxide forms deep flesh-coloured salts with acids. Composition, $Mn\,O$. Atomic weight, 71.

The dioxide is the native ore, and the body largely used in the arts. As already stated, it is our best source of oxygen gas, which is evolved from it when simply heated to redness. Again, chlorine and the chief bleaching compounds are manufactured by its agency. The former is obtained when we heat diluted hydrochloric acid and the dioxide together, the resulting bodies being, manganous chloride, water, and chlorine, as shown in the equation,—

$$Mn\,O_2 + 4\,H\,Cl = Mn\,Cl_2 + 2\,H_2\,O + Cl_2.$$

Manganic dioxide is employed in glass manufactories for overcoming the green tint of ordinary glass; but if too much be used, an amethyst colour is produced, as in the old French plate-glass; this is said by some to be an optical, and not a chemical effect. It is due, however, to the formation of a portion of sesquioxide, or manganic oxide, and the tint of the amethyst itself is said to depend upon the latter body. Manganic dioxide is also the base which gives a deep brown colour in enamel, or glass-painting.

For these finer uses it must be specially prepared, for which purpose Berthier gives a very good method. He heats manganous nitrate to dull redness. This drives off the nitric acid, and at the same time converts the residue into a mixture consisting of dioxide, with a small percentage only of the original protoxide. This latter is dissolved out by some fresh boiling nitric acid, the cake having been previously powdered. Lastly, the resulting powder is washed, and then again heated to low redness, keeping it constantly stirred. It is a very dark brown powder. Composition, $Mn\,O_2$. Atomic weight, 87.

There is a sesquioxide or manganic oxide of a composition between the protoxide and this dioxide, viz., composed of $Mn_2\,O_3$. This is the residue left after distillation of oxygen from the latter. It is also found native. It is a feeble base.

Then there is a red oxide, which has a composition between the protoxide and sesquioxide. It appears to be a compound of these two, having the formula $Mn\,O, Mn_2\,O_3$.

Lastly, there are two oxides having acid properties, viz., manganic and permanganic acids; but they have not been isolated, and are only to be obtained united to a base, or with water. Hence the formula for manganic acid is $H_2\,Mn\,O_4$; and for permanganic $H_2\,Mn_2\,O$ 8.

Discrimination of Manganese.—Manganous salts are commonly of a pale rose colour.

1st. Dihydric sulphide gives no precipitate in manganese solutions if they are acid, and a very slight one if neutral.

2nd. Ammonio-hydric sulphide gives a very bulky, flesh-coloured precipitate in neutral solutions. A slight exposure to air converts this into the brown sesquioxide.

The precipitate is insoluble in excess, but soluble in hydrochloric, or in nitric acid.

3rd. Alkalis or their carbonates throw down white precipitates, and in the case of ammonia this is soluble in excess, and especially so if ammonic chloride be present. Exposure to air soon renders the precipitates by alkalis brown.

4th. Potassic ferro-cyanide gives a white, and the ferrid-cyanide a brown precipitate, from neutral solutions. The former is soluble in acids; and if any iron be present, we get a blue tint from the ferro-cyanide: hence this test is useful in showing the purity of these salts as regards iron.

All these white precipitates become brown upon exposure to air, in a similar manner to the flesh-coloured sulphide.

5th. Mr. Crum's method of detecting manganese is so delicate as to indicate very minute traces. It depends upon the formation of permanganic acid, as shown by the fine red tint of the latter body which is produced. It is thus executed :—Dissolve the compound in a little nitric acid. Then add plumbic dioxide, and boil the mixture, when the least trace of manganese will produce the red tint mentioned.

6th. Any manganese compound may readily be recognised before the blowpipe, by heating it with borax in the oxidizing flame, when a violet bead will be produced. If this be brought into a reducing flame, it is rendered colourless; if simply fused in the outer flame upon platinum wire with a little sodic carbonate, a bluish-green bead of sodic manganate results, which is opaque.

Manganese is estimated by precipitating it from its solutions either as sulphide or as the red or compound oxide, and commonly as this last. For it, the solution of manganese is heated in a large vessel to near its boiling point, and a solution of sodic carbonate is added by degrees, until an excess is present. Then, after boiling for a short time, the solution is poured off the precipitate through a filter; the precipitate next washed by boiling several times in fresh water; next, it is separated by throwing it on a filter. It is then dried, and transferred to a crucible, and ignited. The carbonic acid is expelled, while the protoxide left absorbs sufficient oxygen from the air to become red oxide, or $Mn\,O + M_2\,O_3$. Every 100 parts of this correspond to 72·05 manganese.

Manganese is easily separated from iron. A nitric or hydrochloric solution is formed, and care taken to convert all the iron into a ferric salt. The solution is diluted and added to a quantity of powdered baric carbonate, upon which it is digested for some time. Sesquioxide or ferric oxide is separated, the manganese remaining in solution. (Any alumina present will go down with the iron precipitate.) Next, sufficient sulphuric acid is added to throw down the excess of baryta. Lastly, from the filtered fluid the manganese is separated as above directed, viz. by sodic carbonate, and it is weighed as red oxide.

COBALT.

This metal is not employed in the metallic state, and when reduced it usually contains more or less nickel, for the two metals are associated in cobalt ores, and their separation is only to be effected by protracted manipulation, hence the bulk of specimens of cobalt are magnetic, a property due in all probability to the nickel present. The chief ores of cobalt are, the arsenide, or tin white cobalt, or smaltine, found at Tunnaberg; and the sulpharsenide, or cobalt glance, a compound of cobalt, iron, and arsenic, with sulphur. Zaffre is an impure oxide formed by roasting the ore with twice its weight of quartz sand.

The metal itself may be prepared by first roasting the ore at a moderate temperature, in order to get rid of as much arsenic as possible. It is next dissolved in nitro-hydrochloric acid, evaporated to dryness, and the residue dissolved in water. The solution is then precipitated by dihydric sulphide, thus all metals, except the cobalt and iron go down. After filtering the clear liquid is boiled with a little strong nitric acid, in order to peroxidize the iron, after which potassic carbonate is added to throw the whole down. Then after washing this precipitate, it is digested in oxalic acid, which converts the cobaltous carbonate into an insoluble oxalate, while it dissolves out the iron. After washing the cobalt salt, intensely heating it in a porcelain crucible will at once reduce the metal. The crucible must be encased in a clay one, as the heat must not only be as strong as can be commanded, but must also be maintained from three-quarters of an hour to an hour.

Cobalt is a reddish grey crystalline metal, which fuses at a temperature somewhat below iron. Its specific gravity is 8·95. It is soluble in either of the three acids, sulphuric, hydrochloric, or nitric; exposure to the air oxidizes it completely. Symbol, Co''. Atomic weight, 59.

There are two definite oxides of cobalt, and these again are capable of combination with each other, forming other oxides. But the oxide commercially important is the cobaltous oxide. This is employed in porcelain-painting, and also largely used by glassmakers, enamellers, and others, for imparting the rich azure blue known as cobalt blue. For these uses it is prepared upon a large scale, and by calcining speiss cobalt, the product of smelted cobalt ores. This calcined speiss is treated with hydrochloric acid to dissolve it, after which milk of lime is added to precipitate arsenic and iron. Dihydric sulphide is next passed through the solution to throw down other metals, care being taken that the liquid be well acid, or a black cobalt sulphide would be precipitated by the gas. Lastly, the cobalt compound is itself precipitated by bleaching powder. When the precipitate is heated to redness it forms the 'blue oxide,' but if the heat be carried to whiteness, 'prepared oxide.'

Smalt is a blue colour, employed in the arts for giving a pale blue tint in glass, porcelain, and pottery work, also for paper-staining, and domestic use in the laundry. For these uses ordinary smalt is employed, where the colour is diluted with other admixtures, but for the finer uses of glass-painting a factitious smalt is preferable, where the composition of ordinary smalt is imitated, but wherein pure oxide of cobalt is used.

For ordinary smalt the ore is powdered and levigated, after which it is roasted in such a manner as to render foreign metals as inert as possible, and at the same time to oxidize the cobalt. This effected, it is mixed in the proportion of 4 to 5 parts of ore with about the same weight of pearl-ash, or rough potassic carbonate, and 10 parts of 'sand.' The material termed sand being obtained by heating quartz to redness, quenching it in cold water, and powdering the fragments so got. These are heated very strongly in refractory crucibles so as to vitrefy them. The pots on removal have the glassy mixture ladled off the metallic matters which separate; these latter, termed speiss, consist of sulphides and arsenides of nickel, iron, and copper, which after removal of the smalt are cast into ingots, and worked for the recovery of the nickel. The vitrefied matter is next ground up, the grinding being carried on by stones working in a wooden trough, which has a stream of water flowing through it. The powder is carried thence into a series of settling troughs, the coarser and more coloured particles subside in the ones nearest to the mill, the finer passing on with the washing water to those furthest away. The products are collected and sold under certain trade-marks expressive of its quality.

It will be seen in the above process, that the sand and potassic carbonate form a genuine glass, while another portion of the sand, by union with the oxide of cobalt, forms a silicate of cobalt, and the result is actually glass coloured by cobaltous silicate, which dissolves in it. Good smalt ought not to contain less than 12 per cent of oxide of cobalt; and a very excellent manufacture of this substance is now carried on in Sweden, where it is improved by the previous complete separation of the arsenic and iron from the ore.

The beautiful blue pigment known to artists as Cobalt, or Thenard's blue, is a compound of cobalt oxide with alumina. For its preparation, a solution of cobaltous nitrate is treated with one of potassic phosphate (hydro-dipotassic phosphate). A quantity of alum is also dissolved, and solution of sodic carbonate added. To one part of the first precipitate five of the latter are added, and the gelatinous precipitates well mixed, dried and ignited at a dull red heat in a closely covered crucible in order to exclude the gases of the combustible materials as much as possible, as they would injure the colour of the product. This is further guarded against, by introducing a little mercuric oxide into the crucible, which is decomposed at the heat employed, and fills the vessel with an atmosphere of oxygen, while its mercury volatilizes.

The resulting colour is a beautiful blue powder. The pigment known as Rinman's green is also a cobalt colour. A mixture of zincic and cobaltous sulphates is made; to these a solution of sodic carbonate is added. The precipitate obtained is well washed, and ignited in a porcelain crucible, when the green compound results.

Discrimination of Cobalt.— 1st. Compounds of this metal, when heated in the oxidizing flame of the blowpipe with a little borax, give a very blue bead, so intense that the most minute quantity must be employed in order to obtain the peculiar blue of the metal.

2nd. Dihydric sulphide gives no precipitate in acid solutions, but from neutral ones, part of the cobalt goes down as sulphide, and from alkaline ones the whole falls.

3rd. Ammonio-hydric sulphide precipitates a black hydrated sulphide from neutral solutions, insoluble in excess, or in alkalis; difficultly soluble in hydrochloric acid, but quite soluble by heating in nitro-hydrochloric acid.

4th. Potash or soda in excess precipitates a blue basic salt; this oxidizes on exposure to air, and becomes green. On boiling, it becomes a pale red hydrate.

5th. Ammonia acts as potassa, but excess redissolves the precipitate, which is again thrown down by potassa, or soda, as a blue basic salt. The presence of free acid or ammoniacal salts hinders precipitation by ammonia.

6th. Potassic ferrocyanide gives a brownish green precipitate.

7th. Potassic ferridcyanide throws down a reddish brown one.

Lastly, solutions of cobalt salts when dilute, pass up from rose colour to deep red as they become more concentrated, and from red to lilac and blue, dependent upon the quantity in solution. Many of the dilute red solutions may be changed to blue by heating, the liquid assuming the original tint as it cools.

Cobalt was always formerly estimated as protoxide, but Fre~~sn~~my has shown that it always retains some of the acid, thus this plan is not now used; and of all other methods, that of estimating it as sulphate, either directly or after its precipitation, as sulphide, is of most general application.

CHAPTER XIX.

NICKEL.

Nickel was discovered by Cronstedt in 1751. It is not employed unalloyed, but largely in the formation of the class of alloys known as German silver, electrum, nickel silver, and some others; all of which are alloys where the colour of copper (their basis) is overcome by varying proportions of nickel and zinc added, for when alloyed with copper, nickel has the extraordinary power of whitening such alloys. In cases where the metal is made for founding purposes, a very small percentage of lead is also included.

There are several ores of nickel, but the two from which it is largely obtained are Speiss and Kupfer-nickel. Speiss is a residue from the manufacture of smalt (see page 482), and is a very impure nickel arsenio-sulphide. It contains besides an average of about 48 per cent of nickel, from 1·5 to about 4 per cent cobalt, and varying quantities of some of the following metals, namely, iron, copper, bismuth, magnesia, antimony, and arsenic; and also some sulphur. Berthier gives an analysis of a sample of speiss, as follows:—Nickel, 49 per cent; cobalt, 3·2; copper, 1·6; arsenic, 37·8; antimony a trace, and with these was 7·8 sulphur, and 0·6 of sand.

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Kupfer-nickel is a nickel diarsenide. An analysis of this by Rammelsberg gave the per-centage of nickel as 39·94. The other ores of nickel are Annabergite, an arseniate; Emerald nickel; Millerite, a sulphide; and Eisen-nickelkies, a nickel and iron sulphide.

Some of these ores are found in considerable quantity in Great Britain; arsenide, sulphide, and also kupfer-nickel, in Cornwall; but the Cornish ores seldom yield more than 7 per cent of the metal. The foreign ores worked average from 10 to 15 per cent.

Nickel is very analogous to, and always associated with, cobalt; and as the separation of these two is an operation of some chemical difficulty, it is found necessary, in obtaining this metal even for commercial uses, to have recourse to combined chemical or wet, with more strictly metallurgic or dry processes. Of the ores employed, speiss is the most largely used; but the difficulty of producing the metal from it has led manufacturers to keep the processes secret. Of several, however, which have been described, the following may be taken as illustrating its working:—In all, the first or wet operations are for the production of nickel oxide, and the after dry one for the reduction of the metal from this.

Berthier, in his plan, learns first by experiment how much iron is needed to separate the arsenic in the ore he is about to work upon, as ferric arseniate. He then adds the requisite quantity to the roasted speiss, and dissolves them in aqua regia with a little excess of nitric acid, at a boiling heat. This is evaporated to dryness, and the mass exhausted with water: thus much ferric arseniate is left undissolved, and the remainder is next separated, together with some cupric oxide, by treating the filtrate with sodic carbonate. A white precipitate falls, which should soon turn brown; if it does not, some ferric chloride must be added, for it is thus shown that the quantity of iron was not sufficient at first. The solution must then be again precipitated by sodic carbonate, adding it with care, so as just to throw down the iron compounds; after which dihydric sulphide is passed into the filtrate to precipitate the remainder of the copper; and after the cupric sulphide is filtered out, the nickel and cobalt are precipitated at a boiling heat by means of a fresh addition of sodic carbonate. The nickel and cobaltous carbonates are washed and diffused in water, and an excess of chlorine gas is passed into this liquid, which is subsequently exposed to air, for the evaporation of the excess of chlorine, and then filtered. The nickel will be in solution as nickel chloride, the cobalt or cobaltous oxide filters out, but with it some nickel oxide. Lastly, nickel oxide is precipitated from the chloride by the addition of an alkali.

Thompson digests powdered speiss in dilute sulphuric acid, and adds nitric from time to time, as long as any action is kept up by it. A green solution is produced, from which arsenious acid separates. The latter removed, the liquid is evaporated, and potassic sulphate (equal to half the weight of the speiss) or carbonate added; after which it is concentrated and set aside for crystallization. The double nickel and potassium sulphate is purified by recrystallization, and may then have the nickel oxide separated.

Cloez (Dingl Bd 148, S 206) gives a method wherein he dissolves roasted speiss or kupfer-nickel in powder in concentrated hydrochloric acid. Then to the solution he adds excess of hydrosodic sulphite, and boils until the arsenic acid is reduced to arsenious, and the excess of sulphurous acid driven off. He next passes into the warm solution dihydric sulphide. Thus arsenic, copper, antimony, lead, and bismuth, are separated, and, after standing some time, filtered out. The filtrate is evaporated to dryness, and the residue dissolved in water. Chlorine is passed in. He then adds baric or calcic carbonate, which precipitates iron and cobalt. Sulphuric acid is next added, sufficient to remove any dissolved barium or calcium. After filtering, sodic carbonate is added, which precipitates nickel carbonate, and this is reduced by heating to redness.

The process first published by Louyet, and carried on at Birmingham, may be taken as an excellent one.

He first makes a mixture of speiss, fluor-spar, and chalk, and, having fused them altogether, separates the slag; after which the residue containing the metals is powdered and roasted for 12 hours, so as to separate as much arsenic as possible in the state of arsenious acid. The roasted powder is next digested in hydrochloric acid, and the solution obtained diluted largely with water; after which ordinary bleaching powder (known commercially as chloride of lime) is added gradually, so as to peroxidize the iron present, which is subsequently precipitated by addition of milk of lime, as long as it throws any precipitate down. With this ferric-oxide is associated any arsenic not separated by the above roasting operation.

The liquid, together with the washings of this precipitate, has next a current of dihydric sulphide passed through it, until a portion filtered out will give a black precipitate with ammonia.

The dihydric sulphide precipitates any copper, lead, or bismuth contained, leaving the nickel in solution, together with cobalt. After boiling to get rid of excess of dihydric sulphide, enough lime is added to neutralize any acidity, and now an addition of bleaching powder will peroxidize the cobalt; and upon again filtering the solution, the nickel may be obtained by the addition of milk of lime; it falls as a hydrated protoxide.

The nickelous oxide obtained by any of the above processes is reduced on the large scale by heating very strongly with powdered charcoal in fire-clay cylinders; these are set upright in the furnace and charged from time to time with square masses of the dried oxide and charcoal; the reduced metal sinks to the bottom, and is occasionally removed at openings made for the purpose, and at the same time fresh material introduced at the top.

There are several methods of obtaining pure nickel, and of these Deville's may be employed. He dissolves commercial nickel in hydrochloric acid, boiling the solution to dryness, the residue is digested in water, thus the ferric oxide is left. Dihydric sulphide is then passed in to separate the copper present, the solution being diluted for the purpose. It is then evaporated, and when sufficiently concentrated, oxalic acid is added, thus nickel oxalate is precipitated; this is heated intensely in a lime crucible with a well-luted cover, so as to exclude air, thus the carbonate oxide formed by the decomposition of the oxalic acid reduces the metal itself.

Properties.—It is a white metal, inclining to steel-grey, very hard, and susceptible of a high polish; it is ductile, and very tenacious; when pure, it is malleable, but this property is much diminished by the presence of carbon; it is capable of welding, is magnetic, and has a specific gravity of 8·82 when hammered; it is slowly soluble in sulphuric or in hydrochloric acid—freely so in nitric or in aqua regia. If heated strongly in the air, it is oxidized. Symbol, Ni″. Atomic weight, 59.

There are two oxides of nickel analogous in composition to those of iron, namely, a protoxide and a sesquioxide.

The first or nickelous oxide is precipitated from a nickel salt by a fixed alkali, by which means it falls as a bulky pale apple-green hydrate—the characteristic colour of salts of nickel. This oxide is again soluble in acids, forming salts of nickel. The water of the hydrated oxide may be driven off at a strong heat, but the anhydrous oxide is best prepared by igniting the carbonate in a covered crucible; it is of a brownish-green colour. Ammonia or ammonic chloride dissolves this oxide, forming darker blue solutions. Its composition is $Ni\,O$. Atomic weight, 75.

The second, or sesquioxide, may be formed by heating the carbonate as in the last case, but gently, and with exposure to air; in this way a black powder is obtained; or in the hydrated state by suspending nickelous oxide in water, and passing chlorine through the liquid. The sesquioxide is insoluble in acids; but upon heating it in nitric or sulphuric acid, salts of protoxide will be obtained. Composition, $Ni_2\,O_3$. Atomic weight, 166.

A chloride having a composition $Ni\,Cl_2$ may be obtained by dissolving the protoxide in hydrochloric acid, and evaporating the solution to dryness. The residue may be sublimed in yellow scales.

There are three sulphides—a subsulphide, a protosulphide, and a disulphide. The principal one—viz., the protosulphide—is not precipitated from nickel solutions by dihydric sulphide, but may be so thrown down by ammonio-hydric sulphide. Thus it falls in a hydrated state, as a black powder. It may also be formed in the anhydrous state by heating nickel and sulphur together; action is very violent, and the combination takes place at a lower point than the fusing point of sulphur.

The alloys of nickel are chiefly those which it forms with copper and zinc, constituting German or nickel silver; these will be considered after Zinc. But it may be here noticed that a small quantity of cobalt increases the ductility of nickel. Arsenic will render it, and its alloys, brittle, and disposes them to atmospheric oxidation. Iron and lead also tend to render nickel brittle, both alone and in its alloys.

Discrimination of Nickel.—1st. Dihydric sulphide causes no precipitate if the solution of the nickel salt be acid; but if acidified merely by a vegetable acid, or the solution be quite neutral, partial precipitation will take place. And in the case of a neutral solution entire precipitation takes place by long-continued action of the gas.

2nd. Ammonio-hydric sulphur gives a black precipitate. This sulphide is slightly soluble in excess, and will give a brown tint to the solution. Nickel sulphide is scarcely soluble in hydrochloric acid, but readily so by heating in aqua regia.

3rd. The alkalis throw down green precipitates of hydrated oxide; that formed by ammonia is soluble in excess. Thus a clear blue solution is formed, to which an excess of potassa added will throw down nickelous oxide in combination with some potassa.

4th. Alkaline carbonates throw down nickelous carbonate of similar appearance to the oxide; this again, is, like it, quite insoluble in the fixed alkaline precipitants, but soluble in excess of ammonic carbonate.

5th. Potassic cyanide gives a yellowish green precipitate of nickelous cyanide, soluble in excess, forming a double cyanide, Hydrochloric acid decomposes this and reprecipitates the nickel cyanide.

6th. Potassic ferrocyanide gives a greenish white precipitate.

7th. Potassic ferridcyanide a yellowish green one.

When heated in the reducing flame of the blowpipe, with a little borax or sodic carbonate, a grey-coloured bead is formed, owing to the reduction of the metal itself; and such a bead may be dissolved, and the metal actually collected by the magnet. With borax in the outer flame, a deep yellow or orange glass is produced while hot, which loses much of its colour as the bead cools down.

In estimating nickel, it is always done as protoxide, and by precipitating the metal by potassa; but, owing to the tendency of nickelous oxide to retain potassa, continuous washing is necessary before we can dry and weigh the precipitate.

Its separation from copper and zinc, as in the analysis of German silver, will be considered in the chapter on Zinc.

The separation of nickel from cobalt is an operation often required, and of some difficulty. Liebig's method is the one now generally used. The solution of protoxide of nickel with protoxide of cobalt must be free from other oxides (except of potassium and sodium if associated). Hydrocyanic acid in excess, and then caustic potass is added, and then warmed until all is dissolved, and it is reddish-yellow in colour. It is then heated to boiling, to expel excess of hydrocyanic acid. A double cyanide of cobalt and potassium is first formed, which is next converted into cobalticyanide of potassium, hydrogen being evolved. The double cyanide of nickel and potassium is unchanged. Some mercuric oxide is now powdered, washed, and added, and the mixture boiled. The nickel is precipitated partly as nickelous oxide, and partly as cyanide, mercuric cyanide being produced at the same time. The nickel precipitate is now washed and ignited, and the residue, being pure nickelous oxide, is weighed and estimated.

Wohler determines the cobalt in the filtrate by first nearly neutralizing by nitric acid. He then adds a solution of mercurous nitrate, as neutral as possible; mercurous cobalticyanide falls as a white precipitate; this washed and ignited, gives pure cobaltous oxide for weighing.

CHAPTER XX.

TIN.

There is written evidence that tin has been known as a metal for more than 2800 years; in fact, nearly as long as gold, silver, or iron. In the early times the supply to other parts of the world was derived chiefly from Britain, and as at the present time from Cornwall and Devon, where it exists in veins as a binoxide, or tin-stone. The mine ore is found in veins running through primitive rocks of granite, porphyry, or clay slate. It is generally associated with arsenical pyrites, and in Cornwall often with copper ores, and also with Wolfram, a tungstate of iron and manganese. And the veins in Cornwall almost always run east and west. The nodular masses, known as stream tin, and found in the beds of rivers, as also in alluvial soils, are water-rounded portions of binoxide in a very pure state. And the same ore at times occurs crystalline, in forms belonging to the right prismatic system. Tin is also found in smaller amount as tin pyrites, wherein again it is associated with ferric and cupric sulphides. British tin, with that from the Island of Banca or Straits tin, now constitutes the great bulk and best qualities of the metal; but it is also found in Austria, Siberia, Saxony, Bohemia, America, both in the South and in the States, Mexico, and Australia.

In the year 1860 Cornwall and Devon produced 10,500 tons of ore, which yielded 6700 tons of tin.

Its metallurgy is tolerably simple. The ore is first washed by a good stream of water to separate earthy impurities, and the larger masses and stones broken up, it is sorted as to its quality and association with other metals. If it contains Wolfram it is specially treated; if arsenical or iron pyrites, they are cast away, and copper pyrites is treated for reduction of the copper. The tin ore is itself divided into three classes, as to its richness. A first or richer portion constituting 'best work' being thus separated from a second or intermediate quality, and these again from the third or very poor ore. After this classifying it is powdered in a stamp-mill. The iron stamps weighing from two to three hundredweight each, being so arranged as to work in a kind of box or trough, through which a stream of water flows during the crushing operation. And into this battery the ore is passed down an incline, and as crushed it is washed out of the trough by a grating or series of holes at its sides and ends. By this the powdered ore is carried away into a succession of tanks, passing first over long narrow inclined troughs, during which passage the ore will again separate into three classes. The richest, being the heaviest part, rests on the first or upper portion of the trough, the poorest passes right away to the lower as tailings, while there will be retained an intermediate quantity of ore, also of corresponding or middle quality. Then, again, in the tanks or reservoirs, the same classification takes place, as the heavy crushed ore will subside at once in the first, the lighter passing onwards into others, while the comparatively very light matters are carried still farther, and carrying with them but little ore, constitute slimes.

A similar separation of this kind, depending upon gravity, is effected by throwing the powdered ore in shovelfuls into a large tub or vat, capable of containing 100 gallons of water (or even more). This is called a kieve, or tossing tub. In this the powder is well stirred up, by which means, on leaving it to subside, it forms a top layer of nearly worthless gangue, a middle, which being richer in ore is set aside for another washing, and a lower, which is ready for smelting. During subsidence the separation is assisted by striking the sides of the tub with a mallet.

The intermediate and poorer ore is again washed upon a rack or table so hung upon centres as to admit of its sides being elevated or depressed. It is merely a long table of boards fitted with a shallow rim. It is centred upon its long axis by being hung on two pins or pivots, so that either side may be tilted downwards. The ore and water are thrown upon it by a sloping board at the upper end. They are brushed about so as to spread the ore uniformly to the action of the water, which flows down, as the whole is inclined by a fall of about 6 inches in 9 feet of length. Thus the finer and earthy portions wash down and off the table by a slit at the end, while the heavier ore, brushed to the sides, is from time to time delivered into receptacles formed below on each side; this being effected by letting down the racking table for the purpose.

Pure stream tin needs but crushing and washing in order to fit it for smelting, but mine ore, as containing sulphides of copper and of iron, and also arsenical compounds, must undergo a preliminary roasting previous to actual smelting. For this about half a ton is worked in an ordinary reverberatory furnace, having a bed of about 9 feet long by 5 wide, and with a working door at the back for stirring and rabbling the ore. The heat is kept low so as to volatilize arsenic and sulphur, without at the same time fusing the ore, and the former is condensed and economised by collection in a large flue for the purpose. The roasting occupies from twelve to eighteen hours, and when over, the charge is raked out into a chamber below the bed.

In some works a peculiar kind of reverberatory is used for the last operation, viz. one wherein the bed is formed of a circular plate of iron of about 8 feet in diameter; it is covered with firebrick and arranged so as to be revolved on its centre by means of machinery for the purpose. It revolves very slowly, viz. about four times in an hour, and during this turning, all parts of the ore become equally exposed to the heat, for which object it is kept turned over by the rotation of the bed, under some iron arms suspended from the arch of the reverberatory. The ore is delivered into the centre of the furnace by a hopper, and is gradually passed off to the circumference, whence the calcined ore falls into a proper receptacle below. This apparatus known as Brunton's calciner effects a most complete separation of the volatile matters of the ore, and with little labour required, and also great economy of fuel.

By the roasting operation, the sulphur when present, and any arsenic, which latter is usually associated with the ore, are driven off, and any other metals are converted into light oxides, excepting only any contained cupric sulphide, but this, during the operation, joined with after exposure to air and moisture, becomes sulphate, and is dissolved out by water, and the copper subsequently reduced by iron. The ore is finally washed so as to separate the lighter oxides remaining.

The treatment of tin ores containing Wolfram, or tungstate of iron and manganese consists in fusing them with sodic carbonate, or sulphate, so as to form tungstate of soda, which is dissolved out and crystallized. The ferric and manganic oxides are then readily washed away from the ore, which is left ready for the after operation for reducing its tin.

In practice sodic sulphate is employed rather in excess of the quantity needed to neutralize the tungstic acid estimated as present. The salt is mixed with the ore, together with some powdered coal or charcoal, the latter being for the purpose of decomposing the soda salt. The mixture is heated in a well-closed reverberatory furnace: the carbon, and reducing action of the flame, reduce the soda salt, and sodic sulphide results. Some air is then admitted into the furnace, and thus both the sulphur and sodium are oxidized. The sulphurous anhydride escapes, and the soda takes the tungstic acid of the Wolfram. The mass is removed, and lixiviated with water, after which the sodic tungstate is cystallized out. It has been much used to render light articles of dress non-inflammable, also as a calico-printing mordant.

The tin-stone or roasted ore, as thus prepared, is now ready for the smelter; and, in this country, his operation is always carried on in an ordinary reverberatory (fig. 95), but with a very low arch; the bed *a* is of fire-brick, and peculiar in having a shallow air-chamber *b*, formed under it, which is continued into the bridge: this is to prevent the over-heating of the materials of which the furnace is formed. The charging-door *c*, is at one side, and at the back, and by the side of the flue is a door *d*, through which the charge is worked. Then opposite the charging-door is a channel, closed by a plug during working, but leading to a large iron pot; and into this latter the metal is allowed to flow by this channel, when its reduction is effected. *e* is a stopped opening, which is opened during the time the slags are skimmed off, also when the ore is charging in.

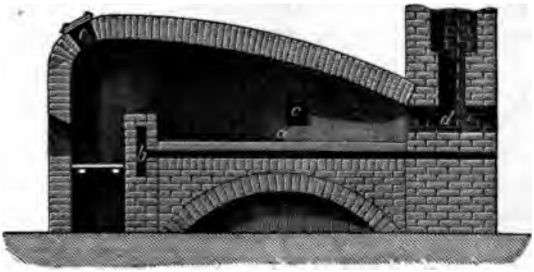

Fig. 95.

In working, the ore is mixed with an average quantity of about 15 per cent of anthracite, and damped, and about 1 ton of this is charged in, a little calcareous flux, as lime, or fluor spar, having been added at the same time. After spreading over the floor, the fire is at first kept moderate, but after a time it is urged in intensity over a period of 6 or 8 hours. The working door is then opened, and the charge well stirred and mixed, and this stirring helps the light metal to subside through the pasty slag formed; after this the doors are again closed, and the heat maintained for a time, when some moist ash is thrown over the surface, and the scoriæ formed raked off. This is reserved in order to separate any grains of metal skimmed with it. A clear bath of metal is thus left in the furnace; the plug is therefore withdrawn from the exit-channel, and the whole allowed to flow into the iron pot, where, after letting it remain for a time, that the slag may rise to the surface, it is lastly skimmed, and the metal ladled into moulds.

In raking the slag or scoriæ, as above stated, from the reverberatory, previous to running out the metal, the top portions are first carefully taken out to within about one fourth of the whole. This being nearly free from metal, &c., is cast away. Part of the remainder is stamped, by which the beads of metal are separated, and the last portions containing some oxide of tin and also metal, are added to the next charge of the smelting furnace. About 7 per cent of the slags is metallic tin.

In Germany tin is smelted much in the same way as iron is in England; and for this purpose a small blast-furnace, as shown in the drawing, is used. A granite body, A, is formed; and in front of this is placed a water-cistern, B; into this the slags of the operation are allowed to flow, while the metal reduced is carried by another channel into the reservoir, C. The body is enclosed above by a hood. The fuel employed is charcoal, and the whole arrangement is worked very much in the way of our iron blast, the prepared ore and fuel being continuously thrown in at the top of the furnace, and again the air being thrown in by similar means; thus the oxygen of the blast with carbon forms carbonic oxide, which reduces the oxide of tin as it passes down; but, although the Germans assert that the product is better, there is much loss of metal compared with the English method, and, moreover, the consumption of fuel is much greater.

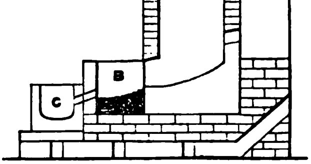

Fig. 96.

The smelting operation does not afford pure tin, but metal in which iron, lead, arsenic, and sometimes tungsten, bismuth, or copper, may exist as impurities. Hence the ingots are subjected to an operation of liquation, in order to separate the pure tin from them. For this they are placed in a reverberatory, and heated very gently: thus the purer tin, fusing first at a low temperature, is allowed to flow off; while the portions associated with the impurities, being more infusible, remain unmelted in the furnace. After the first fluid portions are collected, the remainder is removed, fused, and sold as 'block tin.'

The liquation operation is carried on upon successive lots of ingots, and the purer metal passing from them is allowed to flow into a refining pot: this is heated up by a separate fire, so that the metal may be subjected to a kind of poling operation, somewhat resembling that employed in refining copper, but in this instance performed with a bundle of wet poles, whereby steam is generated upon their contact with the fused and hot tin, and by the escape of which steam, agitation is given to the mass, sufficient to carry impurities to the surface for skimming off. This process, which is called boiling, is carried on for some two to three hours; after which the poles are removed, and the metal allowed to remain at rest, when the denser and less pure portions subside to the bottom. The metal is then ladled out and cast, the first portions constituting refined tin, or bar tin. Sometimes the fine metal is broken up as grain tin, the metal being heated up for the production of the latter to a point whereat it becomes brittle, if pure, and so capable of breaking up readily. This is effected by throwing it from a height down on a hard floor when heated nearly to fusion.

The metal remaining after the removal of the bar or refined tin is cast, and sold also as block tin; but a small quantity at the bottom of the pot is often so charged with foreign metals as to be nearly worthless, or at any rate to need a second refining.

As, after all, commercial tin retains small traces of impurity amounting in the finest kinds to about ·3 per cent, the methods for obtaining chemically pure tin may now be considered. For this purpose good commercial tin may be taken and dissolved in hydrochloric acid: thus hydrogen will be evolved, and the metals all converted into chlorides, with the exception of antimony and arsenic. If either of these be present, it will combine with hydrogen and be evolved as a gas, viz. as antimoniuretted or arseniuretted hydrogen, and some of the antimony may also remain as an insoluble black residue.

Any residue being separated by filtration, the liquid is to be evaporated to a small bulk, and then treated with nitric acid. This will convert the tin into insoluble metastannic acid, a crystalline white body. The whole is now to be evaporated to dryness, and then washed with a little hydrochloric acid; after which it is to be thrown upon a filter, thoroughly washed and dried, and subsequently reduced by mixing it with charcoal, and heating strongly in a crucible, when a button of pure tin will result.

Perfectly pure tin may easily be obtained in small quantities by voltaic action, operating as follows: A concentrated solution of tin in hydrochloric acid is made, and decanted into a beaker; water is next poured cautiously upon it, so as to leave undisturbed the layer of dense liquid, covered with a separate one of water. A bar of tin then placed in the liquid will have the pure metal deposited from the solution, and upon the introduced bar, just at the point of junction of the metallic solution and the water.

Properties.—Tin is a metal very nearly approaching silver in whiteness, and it bears a high polish. Thus a burnisher will give it a beautiful surface, which is not tarnished by exposure to dry air. Although a crystalline metal, it is very soft and malleable, and may readily be beaten into a very tenacious foil, but it is not ductile at ordinary temperatures, and can only be drawn into wire by heating it up to about 212° F.= 100° C. It is readily crystallised by fusing, cooling slowly, and then, pouring away the last fluid portions, eight-sided needles, or else rhombic tables, are so produced; and it may also be separated from stannous chloride by decomposing the latter by means of slow action with the galvanic battery. In such a way it will be slowly deposited upon the negative pole after a few days' action.

Tin will give a peculiar crackling sound if a bar of it is bent, and after a time will become considerably heated by such means: this is produced by the friction of the molecules or crystals upon each other during this bending action. The specific gravity of tin ranges from 7·178, that of the crystals, to 7·295, when well rolled. Tin fuses at 442° F.= 227·8° C.; and casts of this metal contract somewhat upon cooling—hence losing sharpness. When exposed to air during fusion, it oxidizes rapidly, and indeed, burns brilliantly if the heat be carried above the fusing point; but at ordinary temperatures the brilliant white surface of tin is undestroyed.

The three mineral acids act upon it with energy. By sulphuric it is dissolved, and stannic sulphate results, some sulphur separating; hydrochloric acid converts it into stannous chloride—hydrogen being evolved in both these cases. Nitric acid acts more slowly upon it if the acid be concentrated; but, if dilute, its action is very violent, and the tin, in place of dissolving, is converted into a pulverulent but crystalline dioxide.

The alkalis, potash, or soda, when heated with it, act upon it, their water of hydration being decomposed; and thus hydrogen is set free, and the resulting compound is a salt wherein the oxidized tin acts as an acid to the alkaline base.

If a piece of tin be rubbed by the hands, it will communicate a peculiar and disagreeable odour to them: this depends upon the action of animal matter upon the metal. The symbol of tin is Sn^{iv}; atomic weight, 118.

Compounds—Oxides.—Several oxides of tin are described, but the two principal are the protoxide or stannous oxide, and the dioxide, or stannic oxide.

Stannous oxide is the base of the salts of tin. It may be prepared by adding an alkaline carbonate to stannous chloride, when a chloride of the alkali-metal is formed. Carbonic acid escapes, and stannous oxide (or protoxide) falls as a white hydrate. This can be rendered anhydrous, and so preserved, by washing with water recently boiled, and then drying in a retort, but in an atmosphere of carbonic acid or hydrogen. Thus a black, permanent powder is left; but the hydrate will, in its moist state, absorb oxygen readily. It is soluble in excess of caustic potassa, if boiled in it, but after a few days stannic acid will be produced, and some metallic tin deposited. Hydrated stannous oxide is readily soluble in acids, but the anhydrous oxide not easily. Composition $Sn\,O$; atomic weight, 134.

Dioxide of tin, or stannic acid, is capable of two chemical modifications, distinguished by the way in which these two forms will combine with bases; for saturation they require different amounts, and stannic acid the largest. Berzelius describes this oxide under the heads of stannic, and parastannic acids, which have also been later examined and classed by Fremy as stannic and metastannic acids. In both these the tin and oxygen are in the ratio of 1 atom to 2: thus the former is actually a compound of 1 atom of tin with 2 of oxygen, but combined with 1 atom of water, having thus the formula $H_2 Sn O_3$. But in the latter 5 atoms of tin are united with 10 of oxygen, and take 10 of water, which it retains if spontaneously dried; the formula for this is therefore $Sn_5 O_{10}$, $10 H_2 O$. Fremy states that if dried at 212° F. = 100° C. 5 equivalents of this water will be parted with, when the formula will be $H_2 Sn_5 O_{11}$, $4 H_2 O$. By a higher heat, viz. about 266° F. = 130° C. another atom passes off; and, lastly, the oxide will be rendered anhydrous by ignition.

The form called stannic acid is prepared by precipitating a solution of stannic chloride by calcic carbonate—not in excess; thus a gelatinous precipitate falls, slightly soluble in water, capable of reddening litmus, and forming with bases a class of salts called stannates. It is soluble in nitric, sulphuric, or hydrochloric acid.

The variety termed metastannic acid is the product of the ordinary oxidation of tin by nitric acid. The white crystalline powder formed is hydrated metastannic acid. It must be washed with cold water, and dried at an ordinary temperature. This also has distinct acid properties; it reddens litmus, combines with bases, and so forms a class of salts called metastannates. It is insoluble in nitric acid. Dissolves in sulphuric by heat. It combines with hydrochloric, but is not dissolved by it. As before stated, if dried and ignited at a dull red heat, it is rendered anhydrous, and produces the yellow polishing powder known as 'putty powder.' This is much employed in glass and porcelain work, for furnishing a white enamel, for it vitrifies very readily with glass fluxes. For a white opaque porcelain enamel it is mixed with rather more than its own weight of felspar, and fluxed on with a flux of borax, flint, and red-lead. As an opaque enamel, its white colour may be tinted by admixture of other oxides; thus a small quantity of oxides of zinc and iron, mixed with it, will give a brownish yellow, or yellow brown, according to their relative proportions.

Chlorides.—Tin forms two compounds with chlorine, much used by the dyer and calico-printer, under the names of tin crystals or 'salts of tin,' and 'nitro-muriate' of tin. The former is the protochloride or stannous chloride, and may be prepared by dissolving tin in hydrochloric acid by heat (the solution is slow), and when action has ceased, it is diluted with about four times its bulk of water, filtered and crystallized; thus prismatic crystals are formed, which, on dissolving in water, will not, however, give a clear solution without the addition of some hydrochloric acid. This solution is largely used as a deoxidizing or reducing agent; thus, as has been already shown, it readily reduces salts of mercury, silver, gold, and even iron. Mercury is in this way separated for estimation (see page 147); and, again, its action upon iron salts, as also upon gold compounds, is shown (see page 266). For these uses it may be formed in solution; but, if preserved as such, some fragments of tin must be kept in it, or it will deposit a white oxychloride and become stannic chloride. On the large scale it is prepared for the calico-printer by dissolving the tin in copper vessels with care; thus the solution is accelerated by the voltaic action set up between the metals, and the copper is untouched as long as any tin is undissolved. Stannous chloride may be got in the anhydrous state by mixing equal weights of tin filings and mercuric chloride; on distilling the mixture the mercury is separated, and this protochloride is left as a brilliant grey mass. Thus, $Hg\ Cl_2 + Sn = Sn\ Cl_2 + Hg$. Composition, $Sn\ Cl_2$. Atomic weight, 189.

Stannic chloride is a dense colourless liquid which may be obtained by distilling a mixture of one part of tin-filings with four parts of mercuric chloride. Or metallic tin may be fused in a retort (having a receiver attached), and dry chlorine gas then passed over the metal, will produce this chloride which condenses in the cooled receiver. It may be formed in solution by employing stannous chloride, and mixing it with twice the bulk of hydrochloric acid it already contains, and then exposing it to the air for a time; or tin may be at once dissolved in aqua regia, which should be formed with rather an under quantity of nitric acid. This compound may also be crystallised. Composition, $Sn\ Cl_4$. Atomic weight, 260.

Sulphides.—Protosulphide of tin, or stannous sulphide, is formed like the iron compound, by heating tin with sulphur. The metal is heated somewhat above its fusing point, and sulphur is then thrown in. The mass obtained is pounded, and again heated with sulphur in a close vessel, when at last a lead grey, lamellar, crystalline compound is obtained. A chocolate brown hydrate is formed by adding dihydric sulphide to a solution of a protosalt. By heating this, it may be rendered anhydrous. Composition, $Sn\ S$. Atomic weight, 150.

There is a sesquisulphide, and also a disulphide. The latter is a yellow compound, formerly known as aurum musivum, and obtained by mixing an amalgam of 12 parts of tin and 6 of mercury with 6 parts of sal-ammoniac and 7 of sulphur. On heating this mixture in a flask, calomel and mercuric sulphide sublime, and the disulphide of tin remains in brilliant yellow scales. It is used as a bronzing powder by painters. Composition, $Sn\ S_2$. Atomic weight, 182.

Alloys.—Tin readily forms an amalgam with mercury, in fact it may be said to dissolve very easily in the latter metal. The chief use of this amalgam is for 'silvering' looking-glasses. This operation is effected by employing a large perfectly flat stone table, of the size of the glass to be amalgamated, or larger. Upon this a sheet of tin-foil is spread evenly, and it must be without the least flaw or break in its surface, or the latter will show a faulty place upon the glass. This is next covered with clean mercury, by pouring it on, and spreading it uniformly until it lies about $\frac{1}{8}$th of an inch deep. The plate of glass having been perfectly cleansed from grease or impurities upon its surface, is next floated on to the mercury, commencing at one end and sliding it down below the surface of the metal. It is then pressed down by loading it considerably, so as to press out all mercury which does not enter into the composition of a solid amalgam, and which excess of mercury is received in a gutter surrounding the stone. Lastly, after allowing it to rest for a day and a night, it is raised by slow degrees upon its edge, whereby the remaining superfluous mercury drains away. After a few weeks it may be framed, but it is usual to do so in such a way as that the lower end from which it has drained shall come at the bottom of the frame.

The refuse of this operation is the cause of mercury occasionally getting into the market contaminated with tin.

Tin forms a hard but malleable alloy with silver in all proportions, condensation taking place by the mixture. It is very white, but very easily oxidized.

With gold tin forms a malleable alloy, only, however, if the tin be quite pure. Mr. Alchorne has shown that gold containing $\frac{1}{37}$th of tin may readily be rolled, and even coined. Indeed, gold brought to standard by quite pure tin is yet malleable. The specific gravity of this alloy in all cases exceeds the mean, and its colour is rendered of a paler yellow than gold, but with none of the green tint observable in alloys of gold with silver.

Berzelius formed a precipitated alloy of tin and gold, in the condition of a blackish powder, by acting upon a concentrated solution of auric tri-chloride, by one of stannous chloride in excess. This was capable of burnishing, and of fusion into a button.

Tin in filings, heated with spongy platinum in equal proportions, forms a hard and brittle alloy, of a dark colour, and somewhat fusible. Two parts of tin to 1 of platinum has the colour of tin, but is brittle, and it is not until the tin is in the proportion of 12 to 1 that it becomes malleable. Considerable evolution of heat attends the heating of these together; and Clarke states, that if tin and platinum foils be rolled together and heated before the blowpipe, combination takes place explosively.

Tin forms a very brittle alloy with palladium.

The alloys of tin with lead constitute pewter, and also an important class called 'solders;' and, in regard to these, it may be remarked that mixtures of tin and lead are not only more fusible than the mean of their constituents, but they are also harder and considerably tougher. In forming them, the lead should be fused first, and then the tin put in; thus oxidation of the latter is diminished as much as possible; and this object may be also furthered by covering the contents of the melting-pot with charcoal or anthracite powder. When the amount of tin rises a little above one-third of the mixture, and up to two parts of tin to one of lead, the alloy will throw out well-defined circular spots upon its upper surface, when cast in a sheet. This depends upon partial separation of the components of the alloy when in these proportions; but as it becomes yet richer, the spotting gradually disappears, and is as much absent at last as in an alloy containing below the amount of tin above mentioned. Indeed, this appearance affords the plumber the indication of the quality of solder he is making.

Pewter is composed of four parts of tin to one of lead. 'Fine solder,' of two of tin to one of lead. In 'ordinary solder' they are in equal proportions; and in 'coarse' the weight of lead amounts to twice that of the tin. These alloys all expand.

The addition of bismuth to alloys of tin and lead is found to lower their melting point in so extraordinary a degree, as to have given the name 'fusible metal' to this triple alloy. Some of these mixtures melt at points below 212° F. = 100° C., or the heat of boiling water; and the proportions which will give the most fusible compound are two parts of bismuth to one of lead and one of tin; and it will be seen, upon considering the atomic weights of the metals, that these quantities will be just about two atoms of tin to one of lead and one of bismuth. This alloy is largely employed for taking casts, and its value for this purpose is much increased by the fact of its expanding on cooling; and hence giving extremely sharp and well-defined models.

The addition of cadmium lowers the fusing point yet more. Thus the most fusible alloy is one composed of fifteen parts of bismuth, eight of lead, four of tin, and three of cadmium. This forms a silvery white granular alloy which becomes soft at 135° F. = 57° C., and fuses at about 145° F. = 63° C.

An alloy without tin, viz. of seven parts bismuth, six of lead, and one of cadmium, fuses at 180° F. = 82° C. The first formula with tin is known as Wood's alloy. A little bismuth is usually added to the solder employed by pewterers. A good form for this is two parts tin, one of lead, and one of bismuth.

The solders employed for gold and for silver may be here considered. For gold the basis is of course fine gold, and the melting point is lowered by the addition of silver and copper. A good formula for general purposes is 100 parts gold to 40 of silver and 30 of copper. Silver solder is silver alloyed with brass, and a good one is formed by melting 65 parts of silver, and adding 24 of copper, and lastly, 11 parts of zinc; but care must be taken that the zinc is not oxidized, and thus shortened in proportion in the alloy. It is better to form this alloy from the constituent metals, than to use brass as is sometimes done, as the composition of the latter is uncertain.

Tin alloyed with antimony constitutes Britannia metal, the best varieties of which are composed of tin, with just sufficient antimony to give hardness. For this purpose the proportions of antimony may range from 8 to 12 per cent. Some kinds contain also bismuth, zinc, and copper, but these are inferior to that made from the first formula.

An inferior kind is made under the name of 'Queen's metal.' In this 75 parts of tin are alloyed with 8·5 parts of antimony, 8 of bismuth, and 8·5 of lead; but the use of the latter metal is always avoided in good Britannia metal.

The ordinary kinds of type metal are formed of lead, with antimony added in such quantity as to harden it, and enable it to sustain the wear of the press. Twenty parts of antimony to 80 of lead form a good alloy, as such lead fuses readily, and gives sharp casts; but it has been found that if a small amount of the lead is substituted by tin, the type is yet sharper, and resists wear much better. For this 5 per cent of tin is found sufficient. Thus an excellent metal is formed of lead 75, tin 5, and antimony 20 parts.

Tin may be combined with copper in any proportion, and forms with it alloys known as gun, bell, and speculum metals, or bronze; the relative proportions of the constituents determining the character and uses of the alloy. Bell-metal is formed in the proportion of 78 parts of copper to 22 of tin; to these 2 per cent of antimony is occasionally added. In gunmetal for ordnance purposes only 10 per cent of tin is mixed with 90 of copper; but this proportion is often exceeded in metal for engineering uses. Speculum-metal is an exceedingly hard alloy, capable of receiving a very brilliant surface by polishing; whence it is employed for the reflectors of telescopes. It is somewhat brittle. For the best result the copper and tin should be in the proportion of 2 to 1, and a little arsenic improves quality. Thus a good formula is,—6 parts of copper, 3 of tin, and 1 of arsenic.

Genuine bronze is a compound of copper and tin only, but much of this alloy contains zinc also, as in the bronze coin of this country, for example (see Alloys of Zinc). Where metal is intended for the die-press a good proportion will be 93 of copper to 7 of tin. This forms an alloy much harder than copper, and more fusible. It will resist oxidation better, but its hardness renders annealing necessary when it is used for coinage purposes. With respect to the method of annealing, the late Mr. Brande, her Majesty's chief coiner, stated that tempering, or heating and slowly cooling, produces an effect directly opposite to that taking place in steel, and that it renders bronze quite hard and brittle. Therefore it is heated to redness, and quenched in water. After which it is found to be quite soft and workable under the press or in the lathe. Bronze is very liable to have air-holes formed in casting; and its constituents have much tendency to separate upon fusion.

Tin-plate, of which ordinary tin vessels are made, is actually iron coated with tin; but in forming it, the iron having its surface thoroughly cleansed from oxide, is next immersed in a bath of melted tin; consequently, the clean iron surface will be actually alloyed with the latter. The sheets are subsequently dipped in tin a second time, after which any excess deposited is removed by plunging them into a quantity of melted tallow. The superfluous grease is lastly removed by cleansing with bran.

Discrimination of Tin.—1. When a tin compound is heated by the blowpipe in the reducing flame, with a corresponding flux, a malleable globule of tin will be afforded. The best flux for the purpose is one of equal parts of borax and potassic cyanide.

2. Dihydric sulphide may produce a chocolate-brown precipitate in a tin salt, or else a dull yellow one. If the former, it will show the solution to have been one of a stannous salt; if the latter, it will indicate the presence of a stannic salt. If the solution be alkaline, precipitation by this reagent will be more or less hindered; and again, it will be prevented by an excess of hydrochloric acid present.

3. Ammonio-hydric sulphide acts in the same way in each case; and the precipitate produced by this reagent is soluble in an excess of an alkaline sulphide.

4. Potassa or soda produces a white precipitate, soluble in excess. If the solution be that of a stannous salt, a black precipitate will fall upon boiling the clear solution; if it be that of a stannic salt, boiling will not disturb it.

5. Ammonia throws down a white precipitate, insoluble in excess, if the solution contained a stannous salt, but soluble in excess if a stannic salt.

6. Auric trichloride is the characteristic test for tin; in a dilute solution it will precipitate the purple of Cassius; if the solution be more concentrated, this precipitate is brown in colour.

7. Potassic ferrocyanide precipitates stannous salts, and the white precipitate thus obtained is soluble in hydrochloric acid.

The estimation of the quantity of tin in a compound is always made by converting it into dioxide, or metastannic acid; and in this way it may be separated from nearly all other metals. Arsenic and antimony are exceptions, and also lead, if the solution of the metals contain sulphuric acid. To effect this separation, a nitric acid solution is made, and then evaporated to a very small bulk: by this the dioxide of tin is thoroughly separated. Next, any foreign metals are removed from it by washing this precipitate well with dilute nitric acid, and afterwards with water. After which it is dried and ignited, so as to render the metastannic acid anhydrous. It is lastly weighed, and every 100 parts indicate 78·66 of tin.

A few examples may here be given of the analysis of compounds containing tin.

Compounds of tin with lead only, as solders, pewter, and the like, are examined by taking an accurately weighed quantity of 25 grains, or thereabout, and dissolving it in somewhat dilute nitric acid; after heating, the tin will be all oxidized. The liquid is then diluted, and the metastannic acid filtered out, washed, ignited, and weighed.

Sulphuric acid is then added in excess to the remaining solution and washings, and the liquid is evaporated down to expel the nitric acid; next, the plumbic sulphate is filtered out and washed, then removed from the filter into a porcelain crucible; the filter is now burned over the latter, so as to add its ash to the lead precipitate, after which the crucible is heated; and, lastly, the plumbic sulphate weighed, whence the quantity of lead is calculated.

Fusible metal, which contains bismuth in addition to the above, may be analysed similarly by solution in nitric acid. Then an excess of ammonia and a quantity of ammonio-hydric sulphide are added: thus the tin is separated, and by digesting it for a time in a flask is redissolved as a sulphur salt, while the sulphides of lead and bismuth remain. These are filtered away from the clear liquid, and washed well with water containing ammonio-hydric sulphide; after which they are dried, and then separated from the filter into a porcelain basin. To this the filter ash is added, after burning; next strong nitric is put upon this, containing also a little sulphuric. Thus the sulphides are oxidized; and by treating them with water, after having evaporated the excess of acid, bismuthic sulphate will dissolve out, leaving the plumbic sulphate ready for washing: this is done by water containing a few drops of sulphuric acid, and afterwards by pure water. It is then dried and weighed.

The solution containing the bismuth is completely precipitated by ammonic carbonate. After standing some time the precipitate is separated, washed, and decomposed by heating to redness in a porcelain crucible. Thus peroxide of bismuth is left for weighing.

Or supposing the fusible alloy has contained cadmium, as in the case of Wood's metal. The treatment of the solution of bismuth and cadmium sulphides, as dissolved in nitric acid, consists in adding ammonia. This precipitates the bismuth just as by the ammonic carbonate. But it retains the cadmium in solution, which is then estimated as directed under cadmium.

Lastly, returning to the sulphur salt of tin, hydrochloric acid is added to its solution. Thus the tin is separated as disulphide; this is decomposed and oxidized by heating in a porcelain crucible with exposure to air, and the oxide of tin remaining may then be weighed. As most specimens of bronze contain zinc, this analysis will be considered under that article.

An amalgam of tin may be analysed by dissolving a weighed quantity of it in aqua regia; when dissolved, a small excess of ammonia is to be added, and then ammonio-hydric sulphide, also in excess: this is digested for a few hours in a covered flask; the result is analogous to the one in the analysis of fusible metal already given, viz. the tin sulphide will enter into the formation of a sulphur salt and will be taken into solution, while the mercurous sulphide remains undissolved: this is filtered out, washed with water containing ammonio-hydric sulphide, and then the filter dried at a low temperature in a close crucible. The mercury may then be weighed and calculated as mercurous sulphide; but if very accurate estimation is desired, in place of thus drying, it must be digested in hydrochloric acid, and chlorine passed through this until all the mercury is converted into chloride. The solution is then filtered, and the mercury estimated by stannous chloride (page 147).

The tin is estimated as in the case of fusible metal, but in both these the crucible in which the tin sulphide is ignited should have a small piece of ammonic carbonate held in it at last, in order to separate any traces of sulphuric acid likely to remain.

CHAPTER XXI.

ZINC AND CADMIUM.

THE ancient Greeks were acquainted with an ore called by them Cadmia, and employed for mixing with copper to form brass. But the actual separation of the metal zinc (or spelter, as it is commercially termed) from this ore is an operation of more recent date. The ores worked are oxide, sulphides, silicates, and zincic carbonate.

Red oxide of zinc is an amorphous ore, but occasionally found crystalline. It is obtained largely in New Jersey, and is shown by Berthier to be comparatively pure oxide, containing 88 per cent zincic oxide, the remainder being made up of iron and manganese oxides. A mass of this ore weighing 16,400 lbs. was shown in the Great Exhibition of 1851.

Blende is a sulphide of zinc, but it always contains more or less iron sulphide. It varies in colour and appearance according to its association: thus, when black, it contains iron sulphide, and is termed black jack; when of a reddish tint, and streaked, it is mixed with plumbic sulphide. It is at times found brown, green, and even yellow. It contains on an average about 62 per cent of zinc with 32 of sulphur, if pure it should contain just 67·03 per cent of zinc.

Native carbonate or calamine is an abundant ore, not only in our country, but also in Belgium, Silesia, and the United States. It contains about 60 per cent zincic oxide and 35 carbonic acid. This, also, is generally associated with small quantities of iron, lead, and manganese oxides. Electric calamine is a basic hydrated silicate.

The separation of the metal from these ores is an easy operation, and especially so in the case of calamine; for zinc is so volatile that it is readily distilled from this, when previously mixed with any carbonaceous reducing agent. But with blende containing foreign sulphides, and more particularly that of lead, it is somewhat more difficult, and requires some twelve hours' roasting to drive off its sulphur. Calamine is first roughly broken up, and then roasted; although this ore is often reduced at once without. The roasting drives off water and carbonic acid, and during this change the mineral will generally become sufficiently crumbled to powder very easily. This done, the powder is next mixed with half its weight of small anthracite; and the charge for smelting is frequently made up of equal parts of calamine and roasted blende, after which it is ready for the reducing operation. In England, a furnace of the construction shown in the outline drawing has formerly been much employed. It is a kind of kiln, of the shape and build of an ordinary glass working furnace; in the centre of this, and raised upon masonry, is a long fireplace, running from front to back, on each side of which is arranged a row of three very large crucibles, A A, often as large as 4 feet high by 2 feet 6 wide, and capable of containing about 3 cwt. of ore, together with the requisite quantity of coal for reducing it. Over these pots a dome or arch is thrown, D; this latter has a series of holes in it, one being formed over each pot, which serves for introducing the charge, luting the pots, &c., and there is a door in the outer cone corresponding to each opening. Each pot is perforated at the bottom, and has a short tube luted into the opening,

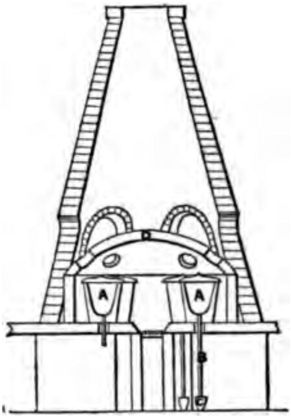

Fig. 97.

as shown in the left-hand pot: this is just long enough to pass through the hearth or table on which the pots stand, down into a cool chamber below. Upon the floor of this is placed a crucible or iron receiver, C, one under each reducing pot, and from the short tubes a long movable piece of iron tube, B, passes down into these. Thus the operation is one of distillation *per descensum*, wherein the volatile product, instead of rising, descends and condenses in the cool receptacle placed below.

The charge of ore and coal having been introduced into each pot, the lids are luted on, and the fire got up, the long tubes, B, being not yet attached; after a full red heat has been attained flame issues at the short tubes; at first blue, from the combustion of carbonic oxide; as this ceases, a brownish flame is seen, due to the combustion of the associated and more volatile metal cadmium, as this fades it becomes of a bluish white colour, indicating the combustion of zinc, the long tube connecting with the under receiver is then put on, and the distilling metal will now condense in drops, and pass down the tubes into the pots below. Any portion of the solid contents of the crucible is prevented passing down the tubes by first stopping them with a plug of soft wood; this, becoming carbonised by the heat, allows of the free passage of the metallic vapours through its pores. Sometimes a loose stopper of coke is so employed. As portions of the distillate pass in the form of powder, and also of zincic oxide, it is necessary to remove the tubes occasionally, and clear them by means of an iron rod, lest by choking explosion should be produced. The distillation will occupy about 36 hours. About 5 tons per week of ore are treated in one of these English furnaces, and with an expenditure of about 12 tons of coal; this will produce about 2 tons of rough metal, which is lastly melted, and the oxide and impurities skimmed off, so as to leave the metal clean.

The Belgian process, as used at the Vielle Montagne Company's works, is now carried out largely in England, as also elsewhere. The ore worked in Belgium is a mixture of carbonate and oxide. This is roasted, but in place of using a reverberatory, as here, a kind of kiln is employed, open at top, and with a series of side openings, at intervals down, by which the products evolved pass into a flue. A high temperature is employed. When the roasting is over, the ore is ground and mixed with small coal, in the proportion of 2 parts of roasted ore to 1 of coal.

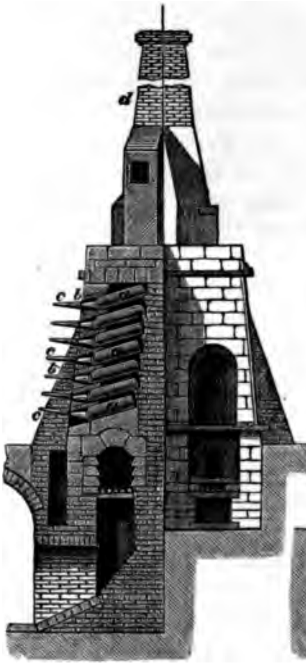

Fig. 98.

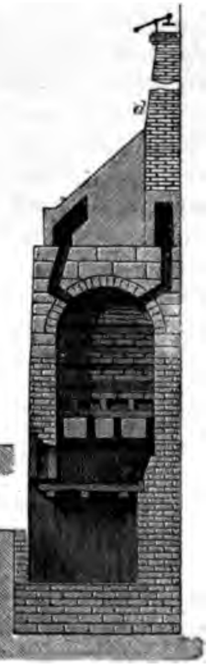

Fig. 99.

This mixture is then distilled in long tubular retorts of fire-clay of about 3 feet 6 inches long by 6 to 8 inches in diameter; these are arranged with an inclination downwards to the receivers, and in a tall furnace, in 8 tiers of 6 each; thus, as the upper rows are farther from the furnace heat, which is below all, the most readily reducible ores are placed in these upper ones, in order to equalize the rate of working of the tiers, and a further attempt to effect this is made by putting larger charges in the lower than into the upper retorts; the charge for the former is about ¼ cwt. each. These furnaces are often built so as to work up to 80 retorts in each bank; and four of these are usually built in one block, with their flues working together into a divided shaft, but each provided with its own damper. Condensation is effected in two tubes to each retort; the first of iron, and of about 1 foot long, tapers smaller towards a second, which is yet more conical, so that its outer end is not more than ¾ of an inch in diameter.

The charge is introduced into the retorts by means of a semi-cylindrical shovel. When all are charged, and the heat has well got up, carbonic oxide will begin to burn at the retort mouths. After this, the condensers being attached and luted on, the zinc itself distils.

These condensers are removed every two hours during working; the outer one contains zincic oxide, which is reserved for working with a fresh charge, the inner one reduced zinc, which is raked out into a ladle, and separated from any oxide, the metal being subsequently cast into ingots. About 12 hours suffice to work a charge of 48 retorts. When the residue has been removed, and the retorts, &c., cleanly scraped out, a fresh charge is worked at once. In this operation about 10 per cent of the zinc is lost, remaining in the residue as a silicate, from its difficulty of reduction.

In Silesia the ores worked are similar to the last; they are first roasted, and then reduced in a retort somewhat like our gas retorts, being a kind of muffle of about 3 feet long by 1 foot 6 inches high, but only 8 inches wide; they are formed of a mixture of fire-clay and old broken-up muffles. After making by hand they are carefully dried, and then annealed, finishing at a good heat. The muffles are supported throughout their length on a muffle-plate. The charge of ore and carbonaceous matter being put in by an opening under the condensing tube and luted up, the distillation is commenced, and the vapour passes by a rectangular condensing tube, and a sheet iron prolongation down into a condens-

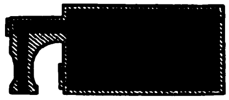
Fig. 100.

ing chamber placed below, and in front of the muffle. This is covered by an iron hearth-plate common to all the retorts. Twenty are arranged in each furnace. Some other methods are employed for the reduction of zinc, but the above are the chief ones, and in all the principle is the same, viz. reduction by carbon and subsequent distillation.

The preparation of pure zinc is an operation of some difficulty, but it is one absolutely necessary where zinc has to be employed for the evolution of hydrogen, in examining for the presence of arsenic by Marsh's test (see page 407); for ordinary zinc is almost universally found to contain traces of arsenic.

Maillet gives a process, in the *Journal de Pharmacie*, which, he says, yields zinc quite pure, as regards arsenic or iron. He first fuses and granulates the metal finely, then covers a crucible at the bottom with nitre, and next puts the metal in, but mixed up with nitre; lastly, covering the whole with another portion of nitre, so that the whole quantity of the latter will thus amount to one-fourth the weight of the zinc. It is now heated until brilliant combustion succeeds, when it is taken out of the furnace, the slag removed, and the zinc poured out.

Various plans have been proposed for re-distilling the commercial zinc, either in the ordinary way or even in an atmosphere of hydrogen; but zinc, after distillation, will be found to retain all volatile impurities; and hence the only way to obtain pure zinc is by solution, and subsequent separation of the impurities.

For this purpose the zinc may be dissolved in pure sulphuric acid: thus zincic sulphate is formed, and an insoluble plumbic sulphate, if that metal were present. The solution is diluted and filtered, and then dihydric sulphide passed through the clear solution; this will throw down any arsenic and cadmium. These are to be separated, and the liquid treated with ammonic carbonate in excess: thus iron is precipitated, and any zinc falling re-dissolved in the excess of the precipitant. Then sodic carbonate is added to the solution filtered from the iron, and the zincic carbonate thrown down separated, washed, and dried; next, by igniting this in a porcelain crucible, pure zincic oxide is obtained, which is to be mixed with its own weight of pure carbon, and distilled in a porcelain retort. The carbon should be prepared for the purpose from loaf sugar. Lastly, if carbon be present, as it may be by the mode of reduction, the pure product must be distilled a second time in order completely to separate it from the metal.

Miller recommends re-dissolving the zincic carbonate obtained as above in pure sulphuric acid, and then decomposing it by electrolysis.

Properties.—Zinc is a bluish-white metal, having a lamellar texture and crystalline fracture; indeed, it is crystallisable in long six-sided prisms. If hammered or rolled, its crystalline texture gives it much brittleness; but it may be extended into sheets by careful rolling when heated to a point between 212° and 302° F., or 100° and 150° C., for it is then perfectly malleable, but becomes again brittle at 392° F. = 200° C. Its specific gravity is 7·146 (7·148 Matthiesen). It fuses at 773° = 412° C.; and when maintained in fusion and heated somewhat above that point, it burns with a blue flame, and is dissipated as zincic oxide. It boils, according to Deville, at 1904° F. = 1040° C. In moist air this metal soon becomes coated with a superficial coat of oxide, which so closely covers it as to protect the metal below most perfectly. It is readily soluble in nitric, hydrochloric, or sulphuric acids, and even in a boiling solution of potash. It shrinks very little on cooling, and hence castings taken in this metal have peculiar sharpness, which property is increased by alloying it with a little tin. Symbol, Zn. Atomic weight, 65.

Binary Compounds of Zinc.—With oxygen zinc forms a protoxide, or zincic oxide, the product of its combustion, and known by old writers as flowers of zinc. The usual method of preparing this oxide consists in throwing granulated zinc into a bright red-hot crucible; but it is apt to be contaminated with particles of metal: these may, however, be removed by washing. It may be obtained in a hydrated state, by dissolving zincic sulphate, and precipitating by ammonia, potash, or soda; but the alkali must not be in excess, or the oxide will be re-dissolved. It is a pure white powder, which, by heating, turns yellow, resuming its original colour upon cooling. Composition, $Zn\,O$. Atomic weight, 81.

Zincic chloride is formed by dissolving the metal in hydrochloric acid, and evaporating to dryness; hydrogen is evolved during solution. If the residue be heated to redness in a tube, it forms a white mass, which, if heat were continued, may be readily distilled. This solid was formerly employed as a caustic in surgery, under the name of butter of zinc. The solution of the metal in acid is now much used, under the name of Burnett's solution: it is powerfully antiseptic; it should be made with as little free acid as possible, but, under any circumstances, it is slightly acid; when very strong, its concentrated solution will deposit portions of zincic oxychloride on dilution. Composition, $Zn\,Cl_2$. Atomic weight, 136.

Zincic sulphide is found native as blende, but zinc and sulphur have but a feeble affinity for each other, and hence this compound cannot be formed by fusing the constituents together. Berthier formed it by decomposing anhydrous zincic sulphate, by heating it to redness in a charcoal-lined crucible: after keeping up the heat for an hour, he obtained a yellow crystalline sulphide. Zinc salts are not precipitated by dihydric sulphide, but a white gelatinous sulphide is precipitated as a hydrate from neutral or alkaline solutions of zinc, by means of ammonio-hydric sulphide. This is soluble in acids, and is readily oxidized by the air. Composition, $Zn\,S$. Atomic weight, 97.

Alloys.—With mercury zinc forms a very brittle amalgam, whatever be the relative proportion of the constituents. The metals combine in the cold by adding zinc filings to mercury, and very readily when melted zinc has mercury warmed and dropped into it. The zinc is better cooled down to near solidification before adding the mercury. Zinc amalgams may generally be powdered, and this brittleness is shown even when 5 parts of mercury are combined with 1 of zinc.

Silver and zinc form a whitish, malleable alloy when the proportions do not exceed 2 parts of zinc to 1 of silver. Gold and zinc unite, and by addition of 1 part of gold to 2 of zinc the latter is rendered whiter. Gold rendered standard by zinc (that is, containing 1 to 11) is of a greenish yellow colour, and brittle, and has a specific gravity above the mean. Hellot states that if 1 part of gold be mixed with 7 of zinc, and heated strongly, the whole alloy volatilizes.

Zinc combines with platinum, and also with palladium, and the union in both cases is attended with evolution of light and heat, and hence combination may be effected at a low temperature. Two parts of spongy platinum, with three of zinc, give a blueish white, hard, and brittle alloy, which fuses easily.

Berzelius gives, on the authority of Cooper, an alloy which, he says, so much resembles 16-carat gold that it can be employed with advantage for ornaments. Its composition is 16 of copper with 7 of platinum and 1 of zinc. The two former are fused under a layer of charcoal with a flux of borax, and the third is then added, and mixed. It is very malleable and ductile, but a trace of iron ($\frac{1}{2000}$) with it, much impairs these qualities. It is not attacked by ordinary 'aqua fortis,' at least if not heated to near boiling. It does not tarnish in air.

Zinc and lead alloy in small proportion of one or the other, as they have great tendency to separate. Thus Matthiesen has shown that on mixing equal parts of the metals and allowing them to cool, they separate into two layers, an upper alloy of zinc with 1·2 per cent of lead, and a lower one of lead, with 1·6 of zinc retained. These alloys are malleable, but hard, and the zinc may be distilled from them.

Zinc and copper form brass, and there are two methods of forming this useful alloy. The first is by fusing or 'cementing' copper with calamine. This is effected in crucibles heated upon the hearth of a kiln. The calamine is ground, and at the same time mixed with ground charcoal or coal, in the proportion of 70 lbs. of calamine to 30 of coal.

The crucibles are filled with this mixture, and for every 60 lbs. of it, 40 of rosette copper are forced down in pieces into the pot. Heating is carried on for nearly 24 hours, until fumes of zincic oxide escape at the lutings of the pots; the heating being thus prolonged, and managed so that the copper may slowly fuse at about the rate the zinc is being reduced. Finally, the alloy formed is poured from the dross and cast. It contains about 80 of copper to 20 of zinc; and is employed in a second melting wherein the proportions of zinc and copper needed to give the true brass composition are added.

The second method of forming brass is by mixing the metals zinc and copper in the proper proportions, but it is usual to fuse with them a certain quantity of old brass equal to one-third of the mixture. And in melting, a considerable quantity of carbonaceous matter, as coal or charcoal, is put into the pot to reduce any oxide formed. Without this, there would be great loss of zinc.

Some care too is requisite in fusing zinc and copper for brass; for at the time they unite the temperature rises so much, that almost explosive union takes place. If the copper is melted and the zinc added, it must be at as low a temperature as will maintain the copper in fusion. But in the ordinary way when old brass is employed, that is put in the bottom of the pot and upon it zinc, copper, and powdered coal in alternate layers, finishing with a good layer of coal. Fusion and alloying then take place after about four hours of heating.

The colour of brass is a golden yellow, and it should have a clean fine-grained fracture. With a very small quantity of zinc, copper is rendered of a paler red, and it gradually passes to yellow as the quantity is increased, becoming brightest when the metals are in equal proportions. The best brass is formed by union of 2 atoms of copper to 1 of zinc, or 64 per cent of the former to about 36 of the latter. Brass of 75 parts of copper to 25 zinc fuses at 1750° = 954·4° C., and the larger the amount of zinc the more fusible the product. A small quantity of lead in brass will injure its wire-drawing qualities, but about 2 per cent much improves its working in the lathe, by diminishing its toughness. For wire-drawing, fine or 'virgin' brass is used. It is cast into ingots of 2 feet long and 3 inches by ¾ inch in section. These are rolled, and then slit up by a circular saw into square lengths of about

¼ inch each way. The squares are drawn, and after rounding, the wire when drawn fine enough is wound on a drum, of about 2 feet diameter, and drawn at pretty quick speed.

A little tin increases the hardness of brass. When the zinc is in excess, it becomes very brittle, and the most brittle kind is that composed of 2 atoms of zinc with 1 of copper. Ordinary malleable brass is also rendered brittle by heating or annealing, and old brass wire will at times become perfectly brittle from having assumed quite a crystalline state internally. Brass may be much hardened and condensed under the hammer. Its great malleability is shown in Dutch metal, which is merely brass with a large proportion of copper, and which beats into leaf, not much thicker than ordinary gold leaf.

What is known as mosaic gold is actually a good form of brass: it is made by fusing equal weights of copper and zinc, and then adding zinc by degrees, until, passing through various tints of yellow, red, and purple, the fused alloy is quite white. This assumes the colour of fine gold upon cooling, and preserves an unoxidized bright surface. Pinchbeck, Manheim gold, Similor, Bath metal, and Prince Rupert's metal, are all brass of various compositions, and are employed for ornamental uses.

Muntz's, Sterro, Gedge's, and Aich's metals are all similar alloys, but employed for larger work. The first, containing a large percentage of zinc, is much used for ship-sheathing in place of copper. By heating it becomes quite malleable; its cost is much less than copper, and it does not foul so much; its composition ordinarily is, 60 copper, 40 zinc, and about ·75 to 1 of lead.

Gedge's alloy is very similar, but in place of lead contains 1·8 per cent of iron, and Sterro metal about twice that percentage of iron, and also about 1·5 of tin. The first is a very ductile and malleable alloy, especially when heated, and the second very tough. Aich's metal is 60 copper, 38 to 40 zinc, and 1·8 to 3 of iron.

Two parts of brass to 1 of zinc form the best solder for brass.

Pure bronze has already been described (page 506), but much bronze contains zinc also. In our coin the quantity is small, for it is a compound of 95 parts of copper with 4 of tin, and only 1 of zinc. But in some of the old Roman bronzes the proportion is so large that they become really brass. Church (in the *Chem. Soc. Jour.* for 1865, vol. xviii. p. 215) gives the four analyses of these bronzes, here transcribed:—

	1.	2.
Copper	84·27	84·90
Zinc with a little Iron	14·70	13·00
Tin	2·36	1·03
Lead and impurities	0·0	1·07
	101·33	100·00

	3.	4.
Copper	86·49	88·19
Tin	6·76	3·64
Zinc	1·44	9·13
Lead	4·41	0·0
Loss and Oxygen	·90	0·0
	100·00	100·96

No. 1 was of a beautiful rich gold colour, and quite untarnished when the earth was washed off it; this and No. 2 were dug from the Main Drainage Works in London. Nos. 3 and 4 were portions of armlets, No. 3 having been broken, and mended at the period of its use, showing the injurious effects of lead in such alloys.

The alloys known as nickel silver, or German silver, as also the Chinese pakfong and tutenag, are formed of copper with nickel and zinc: a very good quality is made, according to Miller, by 51 parts of copper with 30·6 zinc, and 18·4 nickel; this is in the ratio of Cu 5, Zn 3, and Ni 2 atoms. But if the zinc is in any large proportion above the amount of nickel, the alloy becomes yellowish and brassy. Where, however, it is intended for electroplating, for which purpose it is now very extensively manufactured, the proportion of nickel may be low as in the formula just given. The analysis of the better and whiter metal is given at No. 1 in the table following; No. 2 is an excellent one of pakfong; No. 3 is tutenag; No. 4 an alloy of German silver for rolling; and lastly, for casting, No. 1 would be used, but with about three per cent lead added.

	1.	2.	3.	4.
Copper	50	40·4	45·7	60·0
Nickel	25	31.6	17·4	20·0
Zinc	25	25·4	36·9	20·0
Iron	00	2·6	0·0	0·0
	100·0	100·0	100·0	100·0

In forming German silver the copper and nickel must be first melted, and then the zinc added to prevent oxidation of the latter as far as possible; but the infusibility of the nickel necessitates the use of a rather high temperature, and hence much loss of zinc; this should be compensated for as far as can be calculated in making the mixture. Sometimes the materials are arranged in layers in the crucible, as in brass casting, and covered with a good layer of carbon. The alloy must be well stirred before pouring, with a porcelain stirrer. It has a crystalline structure, and before rolling it must be well annealed, so as to overcome this as completely as possible. A good solder for German silver is formed of 4 parts of ordinary nickel silver with 5 of zinc.

Iron may be superficially coated with zinc, as readily as by tin. Such a manufacture is now very largely carried on, for producing what is known as galvanised iron. This is effected by first well cleaning the surface of the iron, and then plunging it into a bath of fused zinc, the latter being kept covered with sal-ammoniac, in order to prevent oxidation, as also to dissolve any oxide of zinc formed. The process was at first carried on by depositing the metal by galvanic agency; hence the name: and the author as a pupil, remembers accompanying the late Prof. Daniell to see the operation so carried on upon the large iron chains for Hungerford Bridge, now the Clifton Suspension Bridge. But although iron is easily covered with zinc by the battery, the method first described is now always practised instead.

Zinc and tin will readily alloy, and, when combined in equal proportions, form a white hard alloy, which may be worked as readily as brass. It is, however, not very ductile and malleable, but sonorous and hard.

Discrimination of Zinc.—1. By heating a zinc compound in the blowpipe reducing flame on charcoal, the metal will be reduced, and burn evolving fumes of zincic oxide. If a zinc compound be moistened with a drop of cobaltic nitrate, and heated in the oxidizing flame, the mass will assume a pale green colour without fusion, this is a compound of zincic and cobaltic oxides.

2. Dihydric sulphide gives no precipitate if the solution be acid, if neutral, or acidulated by acetic acid, the zincic sulphide is precipitated.

3. Ammonio-hydric sulphide throws down a white curdy sulphide from an alkaline solution, but it will be slightly coloured if the zinc compound contains traces of other oxides. The zincic sulphide is insoluble in acetic, but soluble in hydrochloric, nitric, or dilute sulphuric acids.

4. Alkalis and their carbonates give white precipitates : with the former, these are of oxide, and soluble in excess of the precipitant ; with the latter, they are carbonates, and the one produced by ammonic carbonate is soluble ; the other two not so.

5. Potassic ferrocyanide gives a white precipitate.

Zinc is always weighed as oxide, which is calculated as containing 80·24 per cent metal. It must be precipitated by potassic carbonate, added in sufficient quantity to decompose any ammoniacal salts if present, as such would prevent the precipitation of the zincic carbonate. The whole is evaporated to dryness, then hot water added, boiled, filtered, and the zinc salt washed, ignited to drive off the carbonic acid, and weighed.

If thrown down as sulphide, after allowing ample time for subsidence, the precipitate is filtered, washed and dissolved in hydrochloric acid, from which it is precipitated by potassic carbonate as before.

Some analyses may here be given, illustrative of its separation when combined with other metals.

Brass is analysed by dissolving a quantity of about 50 grains in somewhat dilute nitric acid. The solution is evaporated to dryness, and the residue dissolved in a small quantity of dilute sulphuric acid. If the alloy contains lead, it will separate as an insoluble sulphate by this treatment, and may be filtered out and weighed. To the clear solution water is added, and then ammonia to neutralisation, and, next, portions of solid hydrate of potassa until the liquid loses its blue colour. It should be in slight, but care should be taken that it is not in too great excess. The cupric oxide thus thrown down is washed with hot water, ignited, and weighed. Lastly, from the clear solution and washings, the zinc is separated by ammonio-hydric sulphide, and the zincic sulphide resulting converted into oxide as above directed.

For the analysis of bronze it is also to be dissolved in tolerably strong nitric acid : thus the tin is converted into insoluble peroxide (metastannic acid), any large excess of acid is evaporated off, and the remaining solution, rendered dilute, is to be separated from the metastannic acid by filtration; the latter is then estimated as described at page 507. The clear solution is next treated with dihydric sulphide, and the precipitated cupric sulphide examined, and its metal estimated as detailed at page 382. Lastly, the solution filtered from the cupric sulphide is to be evaporated to dryness, and the zincic nitrate left, heated to redness in a platinum capsule: thus it will be resolved into zincic oxide, which may be weighed.

If the bronze be composed of tin and copper alone, it is dissolved and the tin estimated as just described; but the copper present is then ascertained by evaporating down the acid solution, and re-dissolving in water, and subsequently precipitating the copper as oxide by potassa.

But the zinc is generally under-estimated by the above plan, as a small portion of it is apt to be carried down by the cupric sulphide; and, indeed, where zinc is in small relative proportion (as in our new bronze coinage, for example, where the quantity of zinc only amounts to 1 per cent, the alloy being of 95 of copper with 4 of tin and 1 of zinc), it is better to estimate the latter by a dry operation : hence in the chief assay office, at the Mint, the plan adopted is to take a second quantity of the bronze, and, after mixing it with exactly twice its weight of pure tin, enclosing it in a small porous carbon pot, furnished with a cover. This is then luted up in an ordinary covered crucible, and strongly heated in an assay muffle for about 8 hours: by this means the metal is so distributed by the tin, that the small proportion of zinc volatilizes; then, after removing the resulting button when cold, the loss it has suffered is assumed to be due to zinc driven off.

In analyzing German silver, the alloy is first dissolved in nitric acid, and evaporated so as to drive off some of the acid in excess; after this it is largely diluted, and dihydric sulphide passed in; the copper is thus precipitated as sulphide, and estimated as at page 382. The liquid and washings separated from the cupric sulphide are next boiled, and evaporated for concentration, and, while still in the boiling state, sodic carbonate added, which throws down the oxides; these are washed, dried, and mixed with 3 parts of sulphur and the same quantity of potassic carbonate, and the mixture fused to thorough incorporation in a porcelain crucible. After allowing it to cool, it is digested in water, and thus the potassium sulphide formed is dissolved, leaving a mixture of sulphides of zinc and nickel. This is extracted by hydrochloric acid, which will dissolve out the zincic sulphide and leave the nickel sulphide. The latter is to be oxidized by digestion in nitric acid, the mixture diluted, filtered, and the nickel precipitated as oxide by means of potassa (see page 490). Lastly, the zinc is separated, and estimated as oxide by means of potassic carbonate, as already described.

CADMIUM.

This metal is quite of recent discovery, dating as short a time since as the year 1818, and made known about the same time by two chemists separately, viz. Stromeyer and Hermann. It is an associate of zinc, although differing from it in many properties, and, as it is obtained chiefly from the calamine and blende ores of zinc, or from the silicate, was no doubt always worked into the zinc in early times. In these ores its amount varies from 1 to 5 per cent. There is, however, a native cadmic sulphide known as Greenockite, and found at Bishopstown, Renfrewshire.

Stromeyer's method of obtaining the metal was a wet one.

He first dissolved the zinc ore in dilute sulphuric acid, supersaturating it by the solvent; the liquid was then precipitated by dihydric sulphide, and the sulphide obtained washed and dissolved in hydrochloric acid, the excess of the latter being afterwards expelled by evaporation. Ammonic carbonate was next added, and the cadmium thrown down as a carbonate. The carbonic acid was driven off from this by heating it to redness; then, on mixing the oxide obtained with well-burned lamp-black, and distilling the mixture from an earthen retort, the cadmium readily distilled over. This is an excellent process.

A dry method of obtaining it is now used at the Silesian works.

In distilling zinc, as already stated (p. 512), the cadmium first comes over as a yellowish brown smoke. This substance is concentrated by heating in a muffle to which an iron receiver is attached. The temperature is kept moderate, thus a certain quantity of zinc is separated, and condenses in the receiver, while the cadmium smoke is deposited in the lower part, and is now of a brown colour. This is removed and distilled with a quantity of powdered coal (about one-tenth) in a small iron retort; thus the metal is reduced and distils over into the receiver, whence it is removed and cast into ingots or small round rods. It may readily be distilled on the smaller scale, from a glass or porcelain retort.

Properties.—The colour of cadmium is white, somewhat between tin and zinc in shade. It is not quite so soft as tin, although soft and flexible, crackling somewhat as tin does in bending. Its fracture is fibrous, it crystallizes readily in octohedra; it may be drawn into fine wire, and also beaten very thin. Its surface will receive a good polish, which is not oxidized very quickly by exposure to air. It fuses at 442° F.=227·8 C., and at a stronger heat, viz. at 680° F.= 360° C., volatilizes and distils. If a crucible be made red-hot, and the granulated metal thrown into it, it burns like zinc, but with a brown flame, the colour being dependent upon the formation of brown fumes of oxide. Cadmium is readily soluble in dilute sulphuric, or in hot hydrochloric acid, with evolution of hydrogen, and it is also quickly dissolved by nitric acid, which is its best solvent. As already stated, when cadmium is added to any fusible alloy, the melting point is further lowered to an extraordinary extent. This is one of the chief uses of the metal, a second being for the production of a beautiful yellow sulphide, used by artists for painting purposes. Its specific gravity is 8·69; symbol, Cd''.; atomic weight, 112.

Cadmic oxide may be obtained by decomposing cadmic nitrate by heat, or it may be precipitated as a hydrate from the solution of a cadmic salt by potassa. If thrown down by ammonia, the precipitate is re-dissolved, and ammonia will dissolve even the anhydrous oxide. This hydrate is a white powder, which will absorb carbonic acid from the air. At a red heat it loses its water, and becomes of a yellowish-brown colour. It may be deoxidized by charcoal at a low red heat. Its composition is $Cd\,O$; atomic weight, 128. There is a chloride corresponding in composition.

Cadmic sulphide. This compound is precipitated in yellow flakes when a salt of the metal has dihydric sulphide or ammonio-hydric sulphide added to it. When thoroughly washed and dried, it forms a valuable colour to the artist, as it is safely combined with other pigments. It is of a fine yellow, inclining to orange. Cadmic sulphide is formed with much difficulty by fusing the proportionals of metal and sulphur together, but easier, by employing the oxide in place of the metal. Composition, $Cd\,S$; atomic weight, 144.

Alloys.—With mercury cadmium forms a somewhat brittle amalgam, which is crystallo-granular in texture; 78 of cadmium may be combined with 22 per cent mercury, at ordinary temperatures. The alloys formed with other metals are generally brittle, and in the case of copper a very small proportion of cadmium will render it completely so.

Tests for Cadmium.—Dihydric sulphide throws down a yellow sulphide from acid solutions: this distinguishes between this metal and zinc. This sulphide is insoluble in alkaline sulphides, also in ammonia, or in potassic cyanide; but in boiling in dilute sulphuric acid it is dissolved. The first reaction distinguishes it from arsenic.

2. Ammonio-hydric sulphide precipitates a similar sulphide, insoluble in excess.

3. The alkalis, potash, soda, and ammonia, throw down the oxide of cadmium as a white hydrate, soluble in the latter, but insoluble in the two former reagents.

4. Ammonic carbonate produces a white precipitate, insoluble in excess: in this, again, it differs from zinc, as the white precipitate so produced in a zinc salt is perfectly soluble in excess of the precipitant. The precipitate falls but slowly from dilute solutions.

Cadmic salts are reduced before the blowpipe, and if exposed on charcoal, and with a little sodic carbonate to the reducing flame, the metal is reduced, but volatilizes; and in passing through the flame oxidizes and is deposited as a ring of brown oxide upon the charcoal.

The estimation of cadmium is always made by precipitating it as a sulphide by means of dihydric sulphide. But it is occasionally estimated as oxide.

CHAPTER XXII.

ALUMINIUM.

In the third division of base metals, the only one remaining to be considered is Aluminium. Its oxide or alumina is, perhaps, of all others, the most universally distributed body upon the earth's surface. It is the base of all clays, and the bulk of the various soils is made up of varying proportions of it, with other earthy, saline, and organic matters.

Where the isolation of metals of this kind has been effected, it has been by the agency of some other one, which has a yet more powerful affinity for the oxygen or other metalloid combined with the former: as, for example, by employing potassium or sodium, whose vapour, passed over some heated binary compound of the metal sought, decomposes it and sets the metal free. Most of them have been obtained by means of the powerful decomposing effects of the voltaic current.

Aluminium is the only one of its division which, up to the present time, has received any useful application, and this but for the manufacture of alloys and of ornamental articles; and in the laboratory it has also been used for forming small weights, on account of its low specific gravity giving them considerable size, and thus rendering them easy to handle. Its preparation was first carried out by Wöhler, about the year 1827, who obtained it by the action of potassium upon aluminic chloride. He placed a small quantity of the former at the bottom of a platinum crucible, and covered it with the chloride; then, after fixing down a cover with some wire, the vessel was heated up slowly at first, but afterwards strongly; and after the violent action which occurs was over, the crucible, with its contents, being placed in a vessel of perfectly cold water, the soluble residues dissolved out, and left the aluminium as a grey metallic powder.

Of late years this method has been so modified and perfected by Deville, that the preparation of the metal, based on his method, is carried on upon a very large scale by Messrs. Bell, of Newcastle. He employs the analogous metal sodium, which is preferable, on account of its lower atomic weight, and easier preparation as compared with potassium. In working upon a small quantity (up to about half a pound of chloride) he operates as follows:—Placing the aluminic chloride in a large tube of refractory potash glass, he arranges the tube so as to admit of heating it strongly, and at the same time passing a current of dry pure hydrogen gas, free from air, through it. The tube then being first gently heated and a steady current of gas kept up over its contents, a quantity of sodium, perfectly dried from naphtha, and amounting to about 200 grains, is put in, contact with the chloride being prevented by the sodium being contained in small porcelain boats or trays, these being placed in the upper end of the tube, which is slightly inclined. Next the sodium is heated so as to fuse it; after which the lower part of the tube is heated so as to sublime the aluminic chloride, the vapour of which, on contact with the fused sodium, is decomposed, and its metal deposited in the trays, but mixed with undecomposed chloride, and also with the sodic chloride formed. At the close of the operation the tube is cooled, the trays removed, and their contents again fused in an atmosphere of hydrogen, and afterwards in a crucible, when the metal is found to subside below the mixed chlorides, and may be removed in a button.

The inclination given to the tube is in order to prevent the aluminic chloride running down upon the sodium, whence such violent action would arise as to produce a heat which would fracture the tube.

Messrs. Bell carry out the operation on the bed of a reverberatory furnace. They work upon sodio-aluminic chloride, 10 parts of this are mixed with 5 of cryolite, or of fluor-spar, both in powder, and with these 2 parts of metallic sodium in small pieces, or ingots. On heating, the whole mass liquefies, and violent action takes place. The furnace is kept as close as possible to prevent influx of air. Action being over, the charge is run out, and the aluminium subsides in the slag; but from the low specific gravity of the metal, it is rather apt to retain portions of slag. The slag is a mixed one of sodic chloride and aluminic fluoride, the latter constituting a bottom layer in the mixture. The sodio-aluminic chloride used is prepared from the mineral Bauxite, the first step being the separation of hydrate of alumina from this substance. This alumina is mixed with sodic chloride and charcoal, and formed into masses, which are heated in earthen retorts to redness, and a current of dry chlorine is then passed over them, by which the double salt is formed, and distils over. As Bauxite is a clay containing a considerable amount of oxide of iron, the aluminium made from it commonly contains some iron.

Properties.—It is a white metal, of a colour between that of silver and zinc, thus inclining to blue; this tint is deepened by hammer-hardening, which treatment also increases its elasticity, bringing it to about the condition of soft iron in this particular It is malleable, and can be rolled, or beaten very thin; it is also very ductile, and capable of being drawn into fine wire; but for this purpose it must be heated up from time to time during drawing, so as thoroughly to anneal it; and care must be used, as the wire becomes fine, not to fuse it. Its great peculiarities are its low specific gravity, which does not exceed 2·67, and is, under favourable conditions, as low as 2·56; also its extreme sonorousness, for a small bar of the metal, when struck by a hard substance, will give the clear ring of glass. Its melting point has not yet been accurately determined, but from the appearance of the heat required, it cannot be less than 1000° F.; it easily crystallizes upon cooling. For its fusion, the manufacturers just mentioned employ ordinary crucibles, and no flux; also a less intense fire than would be employed for silver; but the heating is carried on longer, and the contents of the open crucible stirred from time to time with an iron spatula; and it is cast in metallic moulds, or else moulds of porous sand.

The surface of this metal takes a fine polish, and is not acted upon by the air. Hydrochloric acid readily dissolves it; nitric or sulphuric acids but gradually, even when the metal is boiled in either of them, but by potassa or soda it is easily oxidized. Its symbol is Al'''. Atomic weight, 27·5.

The difficulty of soldering at first impeded the applications of the metal, but Messrs. Bell find that it may be soldered, if the work is prepared, as in ordinary cases, by first 'tinning;' but this operation must be effected by means of the solder itself. Then the tinned pieces are joined together, and exposed to the flame of a gas blowpipe; and for such purposes the apparatus described at pages 89 and 90 is very useful. Small aluminium tools are used by them, as they state that other ones alloy with the metal and colour it to some extent; and flux, also, is injurious, as it attacks the metal and prevents adhesion. As the solder melts suddenly in a complete manner, the friction of the tool must be applied just at the precise moment; hence the use of the table-bellows blowpipe in setting the hands free. A good general solder is composed of copper 4 parts, aluminium 6, and zinc 90 parts; and in making this, the copper is first melted, then the aluminium added, with a little tallow, and the mixture stirred well with a piece of iron; then at the end the zinc is added carefully, so as to avoid its oxidation as far as possible. They give four other formulæ for solders, but advise the use of the above form for general purposes. From the care needed to solder it, it has been formerly proposed to coat it with copper and then solder in the usual way. Lastly, as to its manufacture, it may be turned in the lathe, by first varnishing the surface to which the tool is to be applied with a varnish of stearic acid in turpentine; this prevents its tearing up.

The important alloys of aluminium are the ones which it forms with copper. Copper with from three to five per cent aluminium, forms an alloy of very gold-like appearance, increased by dipping in aquafortis. The alloy of ten per cent aluminium is more like brass, and is apt to tarnish. Some experiments were made at our Mint with the view of employing the alloy for coinage purposes, but it was abandoned from its producing a metal so closely resembling gold in colour.

Aluminium forms hard alloys with silver, and these have been employed for the formation of ornamental articles. It alloys also with tin, and with zinc, but with these gives rather brittle alloys.

It does not amalgamate with mercury.

Alumina is the only oxide of this metal: it may be procured by recrystallizing ordinary alum until purified. A hot solution of the crystals is then made, and potassic carbonate added; the precipitate formed is digested for a time, to decompose the basic aluminic sulphate at first precipitated. It is next well washed, to get rid of the potassic carbonate; after which hydrochloric acid is employed, sufficient to dissolve it. This solution is filtered, if necessary, and the alumina precipitated by ammonia, washed, and ignited.

Alumina is a perfectly white insoluble powder, very hygroscopic. Moist alumina is soluble in caustic potassa, or soda, and very slightly so in ammonia. With acids it combines, forming salts. Corundum, the ruby, and sapphire, are all nearly pure alumina: the two latter are coloured by oxide of chromium. Indeed, the ruby has been artificially formed by Gaudin, by mixing pure hydrate of alumina with potassic dichromate, drying, and then heating in the oxyhydrogen blowpipe flame; and Deville has formed the sapphire by somewhat similar means. Pure alumina is a sesquioxide. Composition, $Al_2 O_3$. Atomic weight, 103.

The basis of all manufactures in pottery, earthenware, fire materials, and the like, is a hydrated aluminic silicate; and the purity of the clay controls the nature of the manufacture; its general composition may be taken at $Al_2 O_3$, $2 Si O_2 + 2 H_2 O$; but it is always more or less associated with foreign matters, the nature of which is commonly indicated by colour: thus blue clay contains organic matters which burn out and leave the clay white, like china; in it 47 parts of silica are combined with 38 alumina.

The red or potter's clay, used for brown ware, contains about 7 per cent of iron, and 2 of lime. Where much lime is contained it constitutes marl.

Pipe-clay is nearly free from iron.

But the most important of these is the one known as kaolin, or porcelain clay, whose average composition is about 36 parts of alumina with 48 of silica; from this the finer kinds of porcelain are made. It is a compound or mixture of quartz, felspar, and mica. The analysis of Chinese kaolin gives 33·7 alumina and 50·5 silica. With these are associated 1·8 of oxide of iron, 1·9 of potassa and soda, 0·8 magnesia, and 11·2 of water.

Clays are all miscible with water, and, although insoluble, may be so thoroughly mixed up with it as to form a very plastic mass, or even a thin cream when the water is in large proportion; the mass not only contracts on drying, but also greatly upon heating; and in the latter case not uniformly: hence, in forming porcelain, some material is added, which, while it diminishes this contraction, at the same time robs the material of its extreme cohesiveness; then, to make up for the latter defect, a flux is employed, which fusing perfectly at the heat employed in the first firing, permeates completely the pores of the clay, and forms a translucent body, sound and sonorous when struck. Such material is called biscuit ware, and on this any colouring oxides are put, a final glaze being fused over the whole, whereby its porous nature is entirely provided against.

Discrimination of Alumina.—1. Dihydric sulphide does not precipitate salts of alumina.

2. Ammonio-hydric sulphide produces a white precipitate of hydrate of alumina, and at the same time dihydric sulphide is evolved.

3. Ammonia or its carbonate throws down a bulky hydrate.

This is white and gelatinous, and only slightly soluble in the precipitant.

4. Potash or its carbonate produces a similar precipitate; this is perfectly soluble in the caustic alkali, but not in the carbonate. Ammonic chloride in excess reprecipitates alumina from its solution in potassa.

x Before the blowpipe an alumina compound, when moistened with a drop of cobaltic nitrate, gives a fine sky-blue bead. Silica gives the same reaction, but the colour is paler, and thus distinguishes it from that of alumina.

Aluminium is always estimated as alumina. The hydrate being precipitated either by ammonio-hydric sulphide, or by ammonia, or its carbonate. This is carefully washed, dried, and ignited before weighing. The precipitate is very gelatinous and retentive, hence the need of careful washing, as also the difficulty of completely removing adherent matters.

Al, does not fuse, blue mass not bead.

CHAPTER XXIII.

MAGNESIUM.

Of the second division of base metals, magnesium only has been used in the metallic condition, and up to the present time, its application has been confined to purposes where intense white light is needed, for on applying a flame to it, it takes fire, and the light produced is brilliant in the extreme, very white and dazzling. Oxidation of the metal, by its combustion, thus produces the white oxide magnesia, in a light pulverulent condition.

The sources from which magnesium may be obtained are most abundant. The first, or magnesian limestone, is a magnesic and calcic carbonate, and constitutes the mineral dolomite. Magnesite is a simple magnesic carbonate. Then its chloride is contained largely in sea-water, and a double chloride with potassium, has lately been found at Stassfurth in Saxony. This, known as Carnallite, is an excellent source of the metal.

Magnesium is isolated by means precisely analogous to those employed for aluminium. It was first produced by Davy in 1808, and after Wöhler's production of aluminium in 1827, Bussy, a French chemist, by a similar method, separated magnesium. After this, Matthiesen and others got it by electrolysis; but Deville and Caron were the first to produce it in considerable quantity, and modifications of their method are now commonly employed for its manufacture upon the large scale. Sonstadt has much improved and simplified it, and so made the preparation of magnesium a remunerative manufacturing operation.

Deville employs magnesic chloride, and to 6 parts of this adds 1 of sodic chloride, 1 of calcic fluoride, and 1 of sodium, in small pieces; these are intimately mixed, and quickly thrown into a heated clay crucible, which is as quickly covered up. After heating this, the mixture is stirred with an iron spatula; the globules of metal reduced brought together, and as the mixture cools, the whole is poured, and the slag subsequently separated from the metal.

Thus crude magnesium is produced, which has next to be purified; this is effected by first fusing it in hydrogen gas, to bring it into a mass; and again, under a flux composed of magnesic and sodic chlorides, with some calcic fluoride. Lastly it is freed from remaining impurities by distilling it in an atmosphere of hydrogen.

The apparatus for this consists of a crucible having a tube passed up and luted into the bottom. It is carried nearly level with the top edge of the pot and passes below into a close iron box. The crucible is filled with crude magnesium, and the air expelled by a current of hydrogen. It is luted up, and distillation carried on, the tube passing down to the box receiver through the furnace bars, thus the vapour passes down it, and condenses in a mass of drops in the cool box below.

As to the source of the magnesic chloride, Sonstadt decomposed 'rock magnesia,' a magnesic carbonate by hydrochloric acid, then evaporated the solution, and finished it by heating in a crucible until perfectly melted, and thus all the water is driven off, when it is packed in air-tight vessels.

But the native double magnesic and potassic chloride, carnallite, is an excellent source of the metal, as it only requires drying and mixing with calcic fluoride and sodium, and decomposing by fusion at a moderate heat. The proportions used are ten parts of carnallite to one of calcic fluoride, and one of sodium. The metal so obtained requires purification by distillation.

Properties.—Magnesium is a white, or bluish white metal, of exceedingly low specific gravity, viz. 1·743, whence it is troublesome to separate from the flux in its manufacture. When heated, it rises in condensable vapour, hence its facility of purification. But it is very oxidizable at high temperatures, and thus the need for an atmosphere of hydrogen when it is in fusion. At ordinary temperatures it is not readily oxidized unless the air be moist. It is tolerably malleable and ductile when heated. Cold water acts slowly upon it, but readily, if even slightly acid. The action of strong hydrochloric acid upon it is so violent that combustion takes place if thrown into it.

Wanklyn and Chapman have shown that towards the halogens magnesium is very indifferent; at ordinary temperatures a solution of iodine has very little action upon it; it may be dipped in bromine without being attacked, and when plunged in chlorine gas, it is not immediately tarnished. They consider that the well-known decomposition of the haloid salts of magnesium, when evaporated to dryness, depends upon this. Symbol, Mn''. Atomic weight, 24·3.

Alloys of a metal so oxidizable at high temperatures as magnesium is are difficult to make, and it is hence requisite that as low a temperature as possible should be employed. Again, its low specific gravity causes it to float upon the surface of a fused metal. Therefore Parkinson* (who has published an excellent paper on this subject, to which the reader is referred for much information) advises the use of some flux free from oxygen to cover the surface of the alloying metals, such, for instance, as a mixture of sodic chloride, and calcic fluoride. Then the magnesium is wired on to an iron rod, by which it can be passed to the bottom of the pot, and stirred in. And as the metal is so volatile, the heat should be lowered as soon as the metals are alloyed. But, as far as experiments have been made, it is found that all these alloys are very brittle, even with the noble metals, or with copper. One per cent in copper is sufficient to produce brittleness, and 10 per cent will render it easy to be powdered.

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* *Journal Chem. Soc.* vol. xx. p. 117.

Magnesium alloys tarnish easily, and they decompose water. Indeed, they seem of little practical value at present.

Wanklyn and Chapman* have shown that, if perfectly clean, magnesium is heated with mercury to near its boiling point, very violent action takes place, and an amalgam 'endowed with very singular properties' forms. An amalgam of one part of magnesium, with 200 of mercury, tarnishes immediately on exposure to air; when moistened with water, swells up, becomes very hot, and, if immersed in water, decomposes it rapidly.

Magnesia is the only oxide of this metal. It forms a snow-white and bulky powder. It is got by decomposing magnesic carbonate by heat, for which purpose it is packed in crucibles and exposed to a pretty high temperature to expel the acid. Magnesia is quite infusible and very slightly soluble in water. It has an alkaline reaction when moistened, and will with water form a hydrate, which exposed to air absorbs carbonic acid, becoming magnesic carbonate. Magnesia is a protoxide of the formula MgO; atomic weight, 40·3.

Magnesic chloride is found largely in sea-water. It is formed artificially by dissolving magnesic carbonate in hydrochloric acid, but on evaporating this, it is partly decomposed, hence it is usual to dissolve 1 part of magnesia in hydrochloric acid, and add 3 parts of ammonic chloride in solution, on evaporating this, and igniting, the ammonic chloride is expelled, and pure magnesic chloride left as a deliquescent salt. Composition, $MgCl_2$; atomic weight, 95·3.

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* *Journal Chem. Soc.* vol. xix. page 141.

CHAPTER XXIV.

METALS OF THE FIRST DIVISION.

Of the metals belonging to the first division, those which have been applied as such have been used as reducing agents; these are potassium and sodium, both of which are obtained by ordinary means of reduction, somewhat varied in each case. One of the metals of this division, viz. the white metal, lithium, is lighter than any other known solid, its specific gravity being only ·593, or little more than half that of water. But the applications of potassium and sodium, in their oxides, viz. potassa, and soda, and their salts, are extremely numerous and important, and their sources are equally extensive with their uses. Thus, potash is a large constituent of felspar; and hence in some countries is found diffused as a nitrate in the soil, this salt being a result of the decomposition of the felspar, by combination of its potassa with nitric acid, also spontaneously formed from organic decomposition. Again, potassa is supplied in abundance from the ashes of plants, which, by lixiviation, afford a mixture of potassic carbonate and sulphate, known commercially as potashes, and as pearlash. Then the supplies of sodium compounds, from the chloride or common salt, are inexhaustible.

As the methods of producing potassium and sodium are identical except in the compound operated upon, they may be described under one process. The salts employed in each case are the carbonates. In operating for making potassium, this carbonate is obtained by a preliminary step, viz., by decomposing potassic bitartrate by calcination, whereby its tartaric acid is decomposed, and the residue in the calcining pot is an intimate mixture of potassic carbonate and charcoal; this is at once broken up into pieces of about the size of a nut, and put into the distilling apparatus for reduction.

For the distillation of sodium, an artificial mixture is made, nearly resembling the potash one in character. Thus, to 60 parts of dry sodic carbonate, 14½ of charcoal are added, and 9 of chalk. These being formed into a paste with oil, are calcined as in the potash operation, when, after cooling rapidly, the mass is ready for distillation.

A good wind-furnace is required for the reduction of these metals. In it is fixed an iron mercury bottle as a retort; and as these bottles, although serving the purpose admirably, are found to burn out rapidly, a protection of lute is applied, or this may be afforded, by sprinkling some glass of borax over the exterior, which, fusing upon it, protects it from oxidation. This retort is supported upon a brick placed endways under each end; thus it will stand at about 9 inches above the furnace bars, and there should be the means of withdrawing the bars on each side of these bricks, by openings in the front (as in the muffle furnace, page 193). The neck of the bottle being arranged just at the inner side of the furnace opening, a short wide tube is screwed into it, of sufficient length to reach well outside the furnace; this forms an adapter of the retort to a receiver. This latter is formed as a flat copper or iron case or box, which can be opened at the top; at one end it terminates in a tubular opening, which fits closely to the retort tube, and at the opposite end an opening is left whereby an iron rod can be passed straight through the apparatus into the retort itself.

For operating, the material is first introduced into the retort, and the latter then arranged in the furnace, but without the receiver attached. The heat is then got up and carried nearly to whiteness, after which the evolution of the metallic vapour, together with much carbonic oxide, takes place, and will inflame spontaneously; the receiver is now connected, and surrounded by cold-water cloths, or even ice at times, when steady condensation of the metal will be effected; throughout the whole operation, however, a steady stream of carbonic oxide will pass out at the open end of the receiver. If this ceases during distillation it is an indication of stoppage of the tube, which must be immediately cleared by passing down an iron rod or wire; and if this be ineffectual in opening a passage, the fire-bars must be very speedily withdrawn, so as to let out the fuel and stop distillation, or explosion will take place.

Distillation being over, the receiver is opened under some mineral naphtha, and its contents removed and carefully kept in that fluid, which from containing no oxygen will preserve it. If the operation has been for potassium, the yield of rough metal should be about one-fourth the weight of the charge; but as it is always contaminated with carbonaceous matter, and at times with certain explosive compounds, it is always re-distilled, and even twice over if found necessary; by this about one-third of the first product is lost.

In the distillation of sodium, metal equal to one-third the weight of material is usually afforded, and Deville, who uses sodium largely in the isolation of aluminium and analogous metals, so completely manages its distillation as to bring the sodium over in continuous drops, just as water is distilled, and so steadily can he maintain this, as even to be able to remove the receiver for a time and allow the metal to drop into a vessel of naphtha placed below, in order to exhibit the rapidity and nature of the operation.

Potassium is seen to be a blueish-white metal, when a fresh-cut surface is examined. This tarnishes even in naphtha, and very quickly on contact with air, being converted by it into potassa. It has so powerful an affinity for oxygen, that when thrown into water it decomposes it, and with such energy as to inflame the hydrogen set free, by means of the heat evolved during oxidation. The hydrogen flame is coloured violet in this case from admixture with vaporised potassium. Its specific gravity is only 0·865, hence it floats upon the water during its decomposition. At ordinary temperatures it cuts like wax, and is of about the same consistency.

It fuses at 144° F. = 62° C., and sublimes below a red heat. Symbol, K′. Atomic weight, 39·1.

Sodium resembles potassium in colour and general appearance, but its oxidized surface is whitish (potassium appearing blue when surface-oxidized). Sodium also decomposes water, but, if this fluid be cold, it is without inflammation accompanying it. Either of these metals will rob an oxidized body of its oxygen, by simple contact with it, themselves being oxidized; hence they are much employed as reducing agents, and particularly sodium, for its atomic weight being less, a less quantity may be employed than of potassium, then again its preparation presents rather less difficulty The atomic weight of sodium is 23, and its symbol Na.

A large use of potassa and soda is for the formation of the different kinds of glass. Analogous to the aluminic silicate already described as constituting porcelain, are the sodic and potassic silicates; these are called glass. Indeed glass may be described as an amorphous transparent salt, wherein silica unites as the acid, with potassa, soda, lime, and plumbic oxide as bases. It is generally more or less colourless; but if it contain traces of other metallic oxides, it will receive the peculiar colour due to the latter. It is, as just stated, amorphous; but if insufficiently heated, and cooled down slowly, it may be crystallised, although this change of molecular condition seems to be due, to some extent, to separation of the silicates of different bases which enter into its formation. Potassic and sodic silicates constitute the more refractory kinds of glass. Such is the composition of the Bohemian potash glass, whose infusibility renders it invaluable for chemical vessels required to sustain strong heat without change of shape, or fusion. This glass is also exceedingly hard upon its surface, as shown by the application of a file, but it is wanting in brilliancy, and besides possessing a greenish tint, is often full of small granular particles.

Ordinary window-glass, known as 'crown glass,' is a mixture of sodic and calcic silicates, or occasionally of potassic, sodic, and calcic; this is much more fusible than genuine potash glass, but much lime has a tendency to diminish its fusibility and increase its hardness. Plate-glass is of the same chemical composition, and differs only in the fact of very pure material being used for its fabrication; and it is cast upon a flat table, the surface being subsequently polished off; thus this surface is softer and more liable to scratch than a natural one.

Flint-glass is a mixture of potassic and plumbic silicates. The latter addition renders the glass very fusible; and as its density is at the same time much increased; by a natural law, its refractive power is correspondingly enhanced; hence the peculiar brilliancy of English flint-glass. The lead also renders the metal (as it is called) very soft and workable, thus admitting of elaborate cutting. The finest kinds of red oxide of lead are employed in the fabrication of this glass.

As the plumbic silicate is in large proportion in the mixture, and its density is very great, the component silicates of flint-glass have always a tendency to separate; hence the great difficulty in regard to optical glass, as flint-glass is always employed as one element in combination for producing achromatic properties. This difficulty has led to a plan of fusing the material, and well mixing by stirring; then, after allowing the pot of glass to cool, cutting up the contained mass in slices, which layers, although more uniform in themselves, increase in density as they are taken lower from the mass.

The common kinds of glass, known as green or bottle glass, are made of much coarser material, and hence are mixtures of potassic, sodic, calcic, and aluminic silicates with such metallic oxides as may have been present with the bases. Thus the green colour of ordinary bottle-glass is due to ferrous oxide.

For the formation of glass a certain quantity of the raw materials is always mixed with a good proportion of broken glass, called cullet. Thus, for ordinary crown-glass, a mixture of fine sand, soda-ash, or rough sodic carbonate, and chalk, is intimately mixed with nearly their own weight of cullet. This mixture is then exposed to a dull red heat, whereby moisture and carbonic acid are driven off, and partial fusion of parts of the material commenced.

The mixture is next transferred to the glass pots or crucibles, and heated to bright redness, and ultimately fused. The whole is then kept in fusion for a considerable time until all air-bubbles escape, and the impurities rise to the surface; those which arise being chiefly insoluble saline matters, which constitute 'sandiver,' and, when skimmed off, leave the metal in a fit state for working.

Although only magnesium, potassium, and sodium have been described, yet the two divisions of metals to which they belong, viz., the second and first, may be briefly examined as to some of their reactions, more especially as to discrimination, and under one general head, as they possess some features in common, although each may most readily be distinguished by certain special characters.

1. They are none of them precipitated by dihydric sulphide, or by ammonio-hydric sulphide.

2. Dividing them into metals of alkalis and of alkaline-earths, the latter only are thrown down by solution of potassic carbonate; for, although one of the former, viz., lithium, is so precipitated, the carbonate formed is easily dissolved again.

Next, taking the reactions of the alkaline earthy metals, viz. calcium, barium, strontium, and magnesium, into consideration, salts of the first, or calcium salts, are distinguished by giving white crystalline precipitates in very dilute alkaline solutions, when ammonic oxalate is added. But such dilute solutions are not affected by sulphuric acid; if, however, they are concentrated, an immediate precipitate of calcic sulphate takes place. If strongly heated in a Bunsen flame, they colour it a yellowish red.

Baric salts afford the same kind of precipitate with ammonic oxalate, but not in dilute solutions. Then, sulphuric acid, or a solution of calcic sulphate, throws down baric sulphate from solutions containing the smallest traces of barium. Barium salts colour the Bunsen flame a yellowish green.

Salts of strontium are precipitated by ammonic oxalate, but, again, only when the solution is strong; they will also be precipitated by solution of calcic sulphate, and are thus distinguished from calcium salts. And again, this reaction with sulphuric acid or calcic sulphate only occurs after the test has been added some little time, and thus its action differs from that occurring with barium. Strontium salts colour the Bunsen flame intense crimson.

Soluble magnesium salts are precipitated by potass, soda, baryta, or lime, an insoluble hydrate of magnesia falling, and potassic carbonate throws down magnesic carbonate, but not if ammonia be present. Indeed, ammonic carbonate will redissolve the precipitate formed.

Ammonic oxalate gives no precipitate in very dilute solutions of magnesic salts. If strong, and no ammonia or ammonic chloride be present, crusts of double ammonic and magnesic oxalates will form.

Sulphuric acid, or soluble sulphates, give no precipitate. Ammonic triphosphate throws down a granular crystalline precipitate of ammonio-magnesian phosphate, soluble in acids.

Hydro-disodic phosphate throws down a similar magnesic phosphate, as a white powder; but if ammonic chloride be first added, a double phosphate of ammonia and magnesia falls, even in very dilute solutions, and here, if the containing vessel be rubbed with a glass stirrer, white lines of the precipitate will form on the parts rubbed.

Magnesium salts do not colour the Bunsen flame. They are distinguished from those of calcium, barium, and strontium, by the difficult solubility of the hydrate thrown down by alkalis, &c.; also by the sulphate being soluble, and thus no precipitate being formed by adding sulphuric acid. Lastly, by the ready formation of double salts of magnesium and ammonium.

Passing now to the first division, and to the three principal alkaline metals — viz. potassium, sodium, and lithium — if it be a salt of potassium we are examining, the addition of a little tartaric acid in solution in alcohol will throw down a sparingly soluble crystalline salt, potassic bitartrate.

If we add to a potash solution, platinic chloride, we have a beautiful yellow precipitate, also crystalline. This is also thrown down in ammonia compounds; but if any doubt exist as to which has caused it, a small portion of the precipitate may be separated and heated to redness. If it be due to ammonia, all will volatilize but the platinum, which is left in a spongy state ; if, however, it results from the presence of potash, a mass of potassic chloride will remain with the reduced platinum.

Salts of soda give no precipitate with platinic chloride, although a double salt is formed ; but this is very soluble, and can only be crystallized out (in delicate needles) by evaporating the solution. The characteristic test for soda salts is potassic antimoniate, which, when added to a concentrated solution, will give a crystalline precipitate of sodic antimoniate.

If a solution contain lithia, this will give a precipitate with potassic carbonate, but slightly diluting and heating the solution will re-dissolve it.

By dissolving salts of the three last metals in portions of alcohol, and inflaming them, potassa will give a violet, soda an intense yellow, and lithia a reddish-purple flame.

CHAPTER XXV.

THE PRINCIPLES OF ELECTRO-METALLURGY.

There are certain forces, known as electro-chemical, which, in conclusion, it will be desirable to examine. By these, metallic solutions are decomposable, and the metal separated; while also, in the majority of cases, we are thus able to mould and shape the deposited metal more minutely than by the mechanical means of fusion and casting (this is well shown in the capability of electrotyping a daguerreotype plate); or, on the other hand, metals may under the action of the same power, be dissolved, and those even which resist most strongly our ordinary methods of solution: showing that affinities so powerful as to remain untouched by general methods of decomposition, are surely and quietly overcome by this force. Nor is its action confined to the production of these more striking effects, but is equally manifested in all cases where metals of different degrees of oxidizability are in contact under favouring conditions.

If a strip of an easily oxidized metal—as zinc, for example—be taken and placed in a vessel containing some dilute sulphuric acid, chemical action is at once manifested, the metal displacing the hydrogen of the acid unites with its radicle, and zincic sulphate results, the action being attended throughout by evolution of the hydrogen of the decomposed acid.

Next, if a similar strip of platinum be immersed in the vessel, and out of contact with the zinc, no action whatever will be manifested upon the platinum, for sulphuric acid is inactive in this case; but if the ends of the two pieces be brought to touch each other *out of the liquid*, a new condition of things is manifested in the solution, viz., all action upon the zinc appears suspended, and the platinum plate is covered with bubbles of hydrogen gas. But, again, by examining the two after immersion and contact, it would be found that the platinum was untouched, and the zinc dissolved as before, notwithstanding appearances to the coutrary, the hydrogen being in some way transferred to the platinum from the zinc, and evolved at the surface of the former.

When zinc is thus employed as the 'generating' plate for voltaic action, it is customary to cleanse its surface by acid, before use, and to rub it over with mercury; by this means an amalgamated surface is obtained upon which the acid has little or no action while the plate is isolated in it, but when it is brought into contact out of the acid with the platinum plate immersed with it; chemical and electrical action is set up as before.

If, in place of direct contact being made between the metals, it is effected through the medium of a metallic wire, the result is the same; and if this wire be brought over, and parallel to a poised magnetic needle, directly the connexion between the plates is made, the needle will be deflected from its natural position as regards the north—an indication that a current of electricity is traversing the wire, and which current experiment has shown to be generated in the liquid at the zinc surface, and, passing thence through the fluid to the platinum, returns by the connecting wire to the zinc; and further, the deflection of the needle to the right, or to the left, indicates most certainly which end of the wire is connected with the zinc, and which with the platinum plate.*

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* The law of these indications may be thus stated:—If the experimenter be looking towards the north—that is, along the line of the needle in its natural position—and the voltaic arrangement be placed so that the platinum plate is near him at the south, and the zinc at the north end, then, on placing the wire above the needle, the deviation of its north pole will be to his left hand, or west; if the wire were below the needle, the north pole would be deflected to his right hand, or east; or, lastly, if the relative position of the zinc and platinum were changed, then the deviation of the needle is exactly reversed also.

Thus it appears that the chemical action commenced at the zinc is accompanied by a current of electricity, whereby, in the particles of liquid situated between the two plates (and rendered a conductor of the current by the addition of the acid), the mutual affinities of their ultimate elements are suspended while they are excited in equal amount between the opposite elements of the adjacent particles; and thus, by the transference occurring along the chain, free atoms of hydrogen ultimately appear at the platinum plate, for the acid radicle passing to and appropriated at the zinc plate, and the particles between these points are said to be in a polarized state.

The action taking place may probably be rendered evident by the following diagrams, where the symbols Zn and Pt represent the metallic plates, and the symbols the elements of the particles intervening between them :—

State of particles in the liquid before the circuit is complete .	Zn	SO_4 SO_4 SO_4 SO_4 SO_4 SO_4 H_2 H_2 H_2 H_2 H_2 H_2	Pt
State of particles after completion of the circuit	$ZnSO_4$	SO_4 SO_4 SO_4 SO_4 SO_4 H_2 H_2 H_2 H_2 H_2	H_2 Pt

During action all chemical changes take place in atomic proportions, and for every 65 grains of zinc dissolved 98 grains of sulphuric acid are decomposed, 2 grains of hydrogen are separated from it and appear at the platinum plate, and the 96 grains remaining unite with the 65 of zinc to form 161 of zincic sulphate; and hence the amount of zinc dissolved, or of hydrogen collected at the platinum plate, may be made the measure of the power of the circuit, or, on the other hand, the extent of the deflection in a magnetic needle will give the same information. Indeed the latter is made, in the galvanometer, just such a measure; and in that instrument the most delicate currents are made to affect the needle, by insulating the conducting wire, so that it may be coiled a number of times round the magnet, by which the latter will be influenced just in proportion to the multiplication of the tu

An arrangement of a single plate of each metal, as hitherto considered, forms a simple galvanic circuit; and the greater the difference in the affinity the two metals exhibit for the acid radicle, the more energetic will be the produced current, showing that its amount is in proportion to the chemical action going on. The second plate acts in removing hydrogen from the first or generating one, which, by its adhesion, would retard action, tending, indeed, to establish a counter current, by virtue of the affinity of the separated elements for reunion. But a voltaic circuit may be formed by employing a single metal, provided it be so arranged as that two fluids can be used, one to act upon each end of the plate, but differing in their affinity for the metal—one being capable of readily combining with it, while the other is comparatively inactive upon it. (See article 'Tin,' page 498).

The function of the second plate in the circuit is well shown when, in place of employing a plate of zinc in its natural state, we amalgamate its surface with a quantity of mercury, as already described; such a plate, when immersed in dilute acid, would at once become covered with bubbles of hydrogen, showing action to have commenced; but these, by close adhesion to the metal, which is much increased by its amalgamation, quite protect it from the further action of the acid. When, however, we complete the circuit by joining the two plates, the gas bubbles are as before, transferred to the platinum plate, and chemical action is kept up upon the zinc while the gas is so removed, but ceases again when contact is broken.

Where unamalgamated zinc is employed, it is true that the evolution of hydrogen will take place from the zinc surface, even after the circuit is broken; but this results from what is called local action upon the zinc, depending upon ordinary zinc containing minute portions of other metals, in points, about the surface of a plate: these will generate small 'local' currents which are however absent, when chemically pure zinc is employed, as much as they are in the case of zinc amalgamated with mercury.

In a simple voltaic circuit the zinc or easily oxidizable metal would be called the positive or generating, and the second or platinum, the negative or conducting plate. If these were of the same metal, and hence possessing the same affinity for the elements of the exciting fluid, no current could circulate, for the tendency to start it from one of the plates would be opposed by force just similar in amount from the opposite plate; therefore two metals must be employed, and the power will then be in accordance with the comparatively low affinity of the second one for the elements above mentioned, whereby this retarding effect is diminished in the same proportion.

A metal may be positive or negative, in a voltaic arrangement, according to the nature of the one forming the second element of the circuit: thus, if a plate of copper be associated with one of zinc, the zinc will be the positive, and the copper the negative metal; but if copper be opposed to platinum, the copper will be positive and the platinum negative, and a feeble current will be started at the surface of the copper plate, and, passing thence through the exciting liquid to the platinum, will re-enter by the metallic contact at the copper.

Berzelius has arranged the principal metals according to their electric properties; and from his table, commencing with the electro-negative, and passing regularly down to the most electro-positive, they take the following order:—Gold, platinum, palladium, mercury, silver, copper, bismuth, tin, lead, cadmium, iron, zinc, aluminium, sodium, potassium.

A galvanic battery is a series of simple circuits; and if, in its arrangement, the connexion between the separate plates be made from the negative to the positive metal alternately, it would be called an 'intensity' battery; but if the whole set of negative plates were connected together, and then the whole of the positive by themselves, the two series would virtually amount to one large plate of each metal, although divided into the number of small ones employed, and distributed through separate cells or vessels. Such an arrangement would be called a 'quantity' battery.

If, in place of making a continuous wire connexion between the plates of a voltaic circuit, as described, it be cut in the centre, and the cut ends immersed in a vessel containing a conducting fluid—

as a solution of a metallic salt, or acidulated water, for example—the electric current will pass, just as it does through the perfect metal wire, but the intermediate particles of liquid between the divided ends, will be decomposed during the passage of the current, and thus in the case of water, its hydrogen and oxygen will pass in opposite directions in the liquid; and if these wires be of a metal incapable of combining with this oxygen, or are made to terminate by plates of such, as platinum plates for example, the oxygen will be evolved at one end, or pole, while the hydrogen escapes at the other. An instrument arranged for the collection of the gases would form a voltameter.

The points or places where the current leaves, and re-enters, are called the poles of a battery. Thus it leaves the arrangement at the platinum or negative plate, but from the function of the connecting wire or plate in the decomposing cell attached to this, it is called the positive pole; by Faraday the anode, and by Daniell the zincode. Then re-entering at the positive, or zinc plate, the wire or pole in connexion with the latter is called the negative pole; by Faraday the cathode, and by Daniell the platinode. Upon the latter, metals will be deposited, and here also alkalis or hydrogen evolved; while at the former or positive pole, oxygen, chlorine, cyanogen, and the acids will be found.

All compound bodies are not capable of electrolysis. But most metallic salts are under certain conditions so decomposable. For example, those where an acid radicle is combined with a metal, or where a metal is in binary combination with a non-metallic element, as chlorine, iodine, bromine, &c.; or where combined with a body like cyanogen (itself a binary compound), and also some other analogous bodies. But the essential in all cases is, that the salt should be in solution, or the body in fusion, so as to form a liquid conductor of the electric and decomposing force. If the electrolyte be a binary compound, the metal appears, as just stated, at the cathode or negative pole, taking the direction of the hydrogen in the simple circuit, while the other element is set free at the anode or positive pole, the point to which oxygen travels.

The origin of the deposition of metals by electrolysis may be traced to experiments undertaken to determine the cause of the great diminution in activity, which was uniformly observed in the Wollaston battery, formerly the common arrangement, wherein zinc-generating plates were opposed to copper conducting ones, both being in the same cell of exciting fluid; and, although these batteries were made of immense size, this falling off of their power very soon followed their being put in action.

This was traced to the reducing power of the hydrogen adherent to the conducting plate, as also to its tendency to produce a retarding current, depending, as before observed, upon the affinity of the separated bodies for reunion. The reducing power also came into play as soon as the cells became somewhat charged with the zincic sulphate formed during action, and by reducing its zinc, it was deposited at the same spot, viz. upon the copper plate, and so diminished action, by rendering the conducting plates more or less generating ones.

Thus it became evident that any means which would assist in the immediate removal of the hydrogen would maintain and increase the power of the battery; and it was found that the addition even of a little nitric acid to the sulphuric would act chemically, and by its own decomposition afford oxygen to the hydrogen, so forming water, the remaining elements of the nitric acid being evolved as nitrous acid.

This fact has been taken advantage of to the utmost by Mr. Grove in the construction of his battery, where the platinum-conducting plates are placed in porous cells, and charged with strong nitric acid, while the zinc or generating plates are placed in a surrounding cell, and excited by dilute sulphuric acid as usual. It is possessed of very great power from the wide separation of the metals used, in their capability for chemical action; while also the hydrogen set free acts directly on the easily-decomposable nitric acid, producing with it water and nitric peroxide.

Bunsen's battery is the same in principle, but carbon plates are used in place of platinum for economy.

Smee argued that as the hydrogen was always more readily evolved from points about the conducting plate, while it appeared to be tied down by the smoothness of its surface, he could by multiplying such points for its evolution, bring it about fully by such mechanical means. And in his excellent battery he has ingeniously effected this very well, by forming a conducting plate of silver, and then depositing finely divided platinum upon its surface. And thus he is enabled to use both plates in one cell with a single fluid, and consequently requires no porous tubes; thus his battery is very handy and workable, and at the same time tolerably constant.

But to Daniell is mainly due the train of experiments and reasoning which led to the results of the present day, and his 'constant battery,' which appeared before Smee's or Grove's, was the first great step towards bringing them about. He found that the addition of a saline solution to the fluid, and of the same metal as the conducting plate, would be attended by its reduction upon that surface, and consequently by its constant renewal. Thus, in a series of zinc, sulphuric acid, and copper, a small quantity of cupric sulphate added will be decomposed during action, and its copper mainly precipitated upon the copper plate, but then the local currents (already mentioned), as arising in the zinc itself, led to the deposition of copper upon the zinc also; and hence, without some means of preventing this, the battery would again tend to become inactive.

But Daniell found that any porous material, as bladder, paper, or unglazed earthenware, while all-sufficient to prevent the mixture of the fluids, yet allowed the current to pass freely; and thus arose his battery, wherein he employed a cylindrical zinc-generating plate, and placed it in a porous vessel of dilute sulphuric acid; this was contained in the centre of an external copper case or cell, which formed the conducting plate, and the latter being charged with a strong solution of cupric sulphate, was constantly being renewed by reduction of the copper from the salt, and by the action whereby the opposing element hydrogen was being removed from the circuit.

During the experiments which led to this conclusion Daniell actually observed that the copper so reduced might be stripped off in some cases in a coherent sheet; and the author, while a pupil of his, remembers well his exhibiting to his class a portion of the metal so removed, as exemplifying the uniformity of the deposit, inasmuch as filemarks existing on the plate on which the deposit was made, were reproduced perfectly upon the precipitated metal. Yet the great application of this fact escaped both the teacher and his hearers, and was rediscovered by Jacobi, and also by Spencer and Jordan, although no doubt the discovery depended upon the facts elucidated during the production of the constant battery.

Many forms and combinations of elements have of late been devised for batteries, but for electro-deposition of metals, what is needed is one capable of affording a sufficient quantity of electricity with moderate intensity. If the latter be too great a good metallic deposit cannot be obtained, for the metal will go down in a granular form, or even in powder. Thus I have produced deposits of gold very analogous to those obtained by the chemical action of reducing agents, simply by the action of an intensity current. On the other hand, a simple quantity arrangement produces the deposit very slowly, but very reguline and adherent to the cathode.

The battery employed in large electro-plating manufactories is generally a modification of the old Wollaston battery of copper and zinc elements, and commonly from one to three or four pairs of plates are found sufficient, but for smaller work about six cells of Smee's are most useful, and especially for silvering and gilding on the small scale; and, moreover, in the best forms of his battery the sets of plates are usually so arranged in a frame as to admit of their being lowered or raised in the acid cells by means of a ratchet-wheel, so as to immerse the plates to any desired extent, according to the battery power required, as also to allow of very speedy alteration or adjustment of power. An operator of much experience, Mr. A. Watt, says, that he has found Smee's far from economical, and somewhat uncertain in its action; and perhaps it is not so useful in large, as for small and delicate operations, for which the author has much employed it, and with uniform success. Watt recommends a very simple battery for all purposes. Each cell is formed by a four-gallon stone-jar, into which he fits a cylinder of very thin copper; from the top of the latter a strip is prolonged for the positive pole. The jar is covered by a wood top, and by a central hole a porous cylinder is put in for a zinc bar as a generating plate. In the top of this a copper wire is cast for a negative pole. The charge for the porous cell is a concentrated solution of common salt, to which a few drops of hydrochloric acid are added. The outer jar is nearly filled with water, to which two pounds of sulphuric, and one ounce of nitric acid, are added. He says that from a single cell a 'considerable quantity of electricity is disengaged, and of sufficient intensity for small operations such as gilding, and so forth.' But for deposition of a large quantity of metal in a given time, several may be used and alternated, or where desirable not to increase intensity, all the coppers and all the zincs, respectively, may be united.

The art of electro deposition of metals now forms a very extensive branch of manufacture, and by it the old methods of plating are almost superseded, and, in addition to many metals, the deposit of alloys, as brass, German silver, or alloys of gold and silver, are readily effected. In depositing gold however, it may be effected by the battery with so small a covering of metal, that it will soon wear off, and the more rapidly from the softness of gold, pure as the deposit is; while, on the other hand, gold laid on by the old amalgam method, or water-gilding, must be laid on tolerably solidly, or it will not stand the heat necessary for driving off the mercury. Hence the latter method is still more or less used for some works.

Two methods of electric manipulation are in use, the one wherein the battery is employed, and the actual operation carried out in a separate or decomposing cell; the other one, where the body on which the deposit is to be formed, is made the negative plate of a simple voltaic circuit, this is called the single-cell operation.

To commence with an example of the latter or more simple method. Suppose it is desired to obtain a fac-simile in copper of a medal or work of art, which will not be injured by immersion in the copper solution. For the single-cell process, an earthenware or glass jar of sufficient size is arranged, with a cylindrical porous cell placed in it at one side. Into the former a nearly saturated solution of cupric sulphate is put, and in order to keep the liquid from becoming weakened by the abstraction of its copper during the operation, a small quantity of the salt in crystals is suspended in the solution, in a colander or a muslin bag: into the porous cell dilute sulphuric acid is put, one part of strong acid being mixed with from seven to nine parts of water. Next the plates are prepared, the positive being a stout strip or rod of zinc, having its surface amalgamated with mercury, and provided with a binding screw upon its upper end; then the medal is adapted, by binding a clean copper wire round its circumference; after which the reverse, and also the edge, are covered with some non-conductor, as a coating of wax for instance, while the surface to be deposited upon is brushed over with a little black-lead; the first prevents the deposit taking place where the wax covers, otherwise the medal would be actually encased in copper, and the second ensures its ready separation from the surface of the medal.

The zinc plate is now immersed in the acid of the inner porous cell, and the medal thus prepared is put into the outer copper solution, then on bending the wire over to the binding screw of the zinc, and clamping the two firmly together, action commences, and the deposit forms over all parts of the medal uncovered by the wax; the operation is then carried on from one to several hours, or even a day or two, according to the thickness of metal it may be desirable to form. When the proper substance has been deposited, the medal is removed, and the deposit taken off, next the waxed and black-leaded surfaces are changed, and the same operation then carried on upon the reverse side.

But it will at once be seen that the relief parts of the medal must be reversed in these copies, therefore the latter have now conducting wires soldered upon them, and are then employed in a similar way as matrices, in which to deposit metal again, which second pair will be exact copies of the original medal.

Now, although the simplicity of the process just described strongly recommends it, and renders it very applicable to operations upon small objects, it is difficult to exercise that control over the nature and rate of deposit which may be easily obtained by employing the battery; hence, for all works upon the larger scale, a separate cell connected with a battery is to be preferred, as affording these facilities, and at the same time enabling the operator to maintain his solution in more uniform condition.

In extensive electro-metallurgic works the decomposing cell is usually a large trough, but for operations of moderate size a large glass or stoneware jar answers best, and particularly for working upon gold or silver solutions, as these require to be kept at a tolerably warm temperature by artificial means during the progress of the deposition. A metal bar carried across, and resting upon the upper edge of the jar, is provided with a binding screw, by which to attach it to the positive pole, or wire proceeding from the first silver plate of the battery. A similar one is placed parallel to the first, and at the opposite side of the jar, this is attached to the negative pole, or wire proceeding from the last zinc plate. These are made capable of regulating the distance between them as desired, for this is one means of controlling the rate of the deposition, Then the jar being filled with a somewhat dilute solution of the metal about to be employed, a plate of the same metal is to be attached to the first metallic bar, in connexion with the positive wire from the battery. Lastly, from the second bar (and negative wire) the article or mould upon which the deposit is to be made, is hung, or indeed any number which the bar will carry, care being taken that all the metallic contacts are perfect throughout, from the last zinc plate of the battery to the actual surfaces of the moulds. The addition of the metallic salt to the decomposing cell, renders it a better conductor of the current, but, as regards the deposit itself, metal for that is continuously supplied by the gradual solution of the suspended plate, which takes place under the influence of the battery current setting free in the liquid the elements for dissolving the anode or positive plate of the decomposing cell.

Thus all connexions being perfectly established, the deposit will proceed. Its rate, and also its texture, however, will be regulated by the following points: 1st. The strength of the solution, and consequent conducting power; 2nd, the temperature; 3rd, the amount of surface of anode immersed in the solution, and consequently being dissolved; 4th, the degree of battery power; and last, the distance between the anode and cathode in the cell.

If these points are well balanced, the formation will be uniform in texture, tough and coherent, and the slower the rate of deposit the harder it will be. But, if the solution be too strong, or the battery power too intense, or if any one of the foregoing conditions be in excess, the deposit will be granular and non-adherent, so as to drop off the mould into the solution. Or it may go beyond this and be thrown down quite pulverulent.

During the operation, and particularly where it is performed by the battery and a decomposing cell, it is necessary to keep the liquid well mixed by occasional stirring, otherwise that portion surrounding the positive plate is apt to become unduly charged with metallic salt, while at the negative plate it becomes comparatively weak. Under such circumstances a gold deposit will be of a dull brown colour, non-adherent, and bad, but on agitation improvement of the deposit is soon evidenced by restoration of a good colour.

For ordinary work the operation should always be commenced with a moderate battery power, and increased as seen to be needful, and the amount of power to be put on may be determined, and apportioned according to the experience of the operator, and judged of by the examination of the deposited metal as it proceeds; but there are cases where extreme care is needed, both as to the nature and amount of deposit, and where consequently more determinate means must be employed to ensure the perfection of the process. Thus it is customary to divide the wire proceeding from the zinc of the battery and interpose a galvanometer needle. Then in working, the battery plates are immersed to just the depth which will deflect the needle to a point, whereat by experience the deposit is known to form in a close and coherent manner.

Before leaving these points of manipulation it may be observed, that without attention to the renewal of its acid some forms of battery will diminish in power, and the operation consequently go on very unsatisfactorily from saturation of the liquid with zincic sulphate; the time for attention to this is indicated by the amount of work which has been done, as also by the state of the zinc plates, and when once the latter have become bare of amalgamation, their solution goes on very far in advance of the amount of work done. Fresh acid must therefore be supplied from time to time; and if, as is sometimes the case, reduction of the zinc has taken place upon the platinized silver of Smee's arrangement, the remedy consists in removing the zincs, and dipping the silvers for a short time in some dilute sulphuric acid, which will cleanse them perfectly.

The solution employed for depositing copper in all ordinary cases is made by dissolving the sulphate of commerce in water, and then adding a small quantity of sulphuric acid. If the solution required is for a single cell, it is made nearly saturated, and the acid subsequently added; but if it be for use in a decomposing cell, a weaker one is employed, made by dissolving a pound of the salt in 7 or 8 pounds of water, and to this it is usual to add about 14 ounces of sulphuric acid.

But this ordinary solution will not serve for depositing upon iron, steel, or any of the more electro-positive metals. This may be effected by employing the double cyanide of potassium and copper,—a salt easily prepared as follows:—Potassic cyanide solution is added to one of cupric sulphate; thus a green precipitate falls, which is to be removed, washed, and dissolved in a solution of potassic cyanide, and, after diluting considerably, is ready for use. Care must be taken not to inhale the gas evolved during the preparation of the cupric cyanide, as it is very poisonous.

As articles of iron or zinc are liable to be soiled by grease or oxide, they must be perfectly cleansed before attempting to coat them. For this (as for similar uses) a strong solution of caustic potassa is used, and may, therefore, be prepared in quantity by dissolving commercial pearlash, and adding half its weight of powdered quick-lime to it. After standing about 24 hours, the clear solution may be poured off for use.

After cleansing iron articles by this, they are to be washed a second time, but with dilute sulphuric acid containing a little hydrochloric also, and, after this, a good brushing with some fine sand, and, lastly, washing with clean water, will leave them ready for coating. The decomposing cell for this operation should be kept at a temperature of about 160° F., or 71° C.; and as the operation is altogether more troublesome than with the ordinary solution, as soon as a good adherent deposit is down, the work may be removed and completed in a sulphate solution in the ordinary way. In order to get the first film from the cyanide solution, the battery power must be considerable, so as to keep up evolution of hydrogen from the iron surface, during the deposition of the copper.

The deposition of gold or silver, as analogous operations may be considered together, and if performed by the single cell process, in consequence of the expensive material we are dealing with, a different arrangement may be made of its parts, especially where the article to be covered is small. The cell may, therefore, be constructed by putting the zinc or positive metal with the sulphuric acid in the external or larger vessel. In the centre of this is put the porous pot, and into this the gold or silver solution, and on connexion of the mould with the zinc plate, action will be carried on just as in the opposite arrangement.

But for silvering or gilding, it is again absolutely essential, in order to obtain a thoroughly adherent deposit, that the surface of the metal to receive it be scrupulously clean; hence the first step, especially with any old metallic surface, consists in well washing it in caustic potassa, and subsequently in clean distilled water. In addition to this, in some cases the article is quickly dipped in nitric acid and washed, or else slightly scratched by a coarse scratch-brush, so as to destroy the perfectly smooth surface which would not afford so firm a hold for the deposited metal as a slightly roughened one.

The solutions either for gold or silver may be prepared by the battery itself, and an ingenious operator (Mr. Ladd) has been for some years in the habit of thus dispensing with all strictly chemical processes in their preparation. He first makes a clean solution of potassic cyanide in distilled water, employing about ¼ oz. of salt to 30 ozs. of water. This is put into the decomposing cell: next the gold, or silver plate or pole, (according to the solution required) is attached to the cell bar connected with the last silver of the battery; then placing a porous pot in the solution in the cell, a sheet of copper is put into this, and connected with the last zinc of the battery; then upon putting the latter into action, the cyanide will be decomposed, and the gold or silver plate slowly dissolved; but as the copper plate, by being placed in the porous pot, is protected from the deposition of the dissolved metal, the latter is taken into solution in the fluid of the cell, as a double cyanide of gold, or of silver, and potassium, and when the porous cell and copper are removed, is ready for use.

The amount of gold or silver so dissolved may be controlled to a nicety by weighing the plate before the operation, and occasionally during its progress, until the proper richness is arrived at. For silver, a solution to work well should contain about 1 oz. of silver in 50 oz., and for gold 1 oz. in 100 will generally be sufficient. This plan of preparing solutions is now used in some of the larger electro-plating works.

But it is at times necessary for single cell operations to prepare the solutions in the ordinary way. The following formulæ will afford good results:—

For silver, a solution of pure nitrate is first made, and potassic cyanide added to precipitate the whole of the silver as cyanide; but the addition must be made cautiously, as the argentic cyanide is soluble in excess of the precipitant. Should too much be added, the precipitate may be recovered by the addition of more argentic nitrate, until saturation is exactly arrived at. Next, separate the precipitate by decantation, and well wash it, and then dissolve in potassic cyanide, in the proportion of about three parts of the latter to one of the silver salt; this is then diluted to a proper strength for use. But, in order to avoid chances of loss by the preparation of the argentic cyanide, the argentic nitrate may be precipitated as oxide (see page 175). This, when well washed, may be dissolved in the potassic cyanide solution as before.

The gold solution is made by first preparing a clear solution of pure auric chloride (see page 265). To this strong solution of potassic cyanide is added, stirring at the same time, brisk effervescence takes place, and a brown precipitate falls. The cyanide is, therefore, added cautiously as long as this takes place. Next, the separated precipitate is well washed, and dissolved in a solution of potassic cyanide, containing about seven parts of the salt for every one of gold in solution. This may now be employed for gilding, although some operators again evaporate to dryness, re-dissolve in boiling water, and filter before using.

In depositing gold or silver, the operation is best performed at a temperature of from 130° to 170° F., or 55° to 76° C. This is conveniently carried out by using an enamelled iron pot of water, and keeping it hot by a ring gas-burner; this forms a water-bath, in which the decomposing cell is placed; and in case of accidental fracture of the latter, forms a clean receptacle for the valuable solution.

The manipulation employed by Messrs. Ladd and Oertling in gilding the Government standard weights, and hydrometers, and the like delicate instruments, may be detailed as affording a good example of the requisite practice to insure perfect workmanship.

The metal being first carefully cleaned by potassa, is immersed in the silver bath (of proper temperature), and the battery plates being lowered in their cells, a thin coat of silver is first given, as it is found that this metal is if anything more adherent, and forms a good foundation for gold: the instruments are removed in a few minutes, and thoroughly brushed [illegible] wire scratch-brush revolved by a lathe; thus the [illegible] metal is thoroughly burnished down, while, at the [illegible] of solution retained under the yet porous coat of silver are squeezed out by this treatment. After a second coat of silver and again burnishing, the work is transferred to the gilding cell, and the operation carried on in the same way, alternately gilding and burnishing until the requisite quantity of metal has been put on. If the work be weighed before and after one of these burnishings, it will be found that little or no metal is taken off, but that it acts just as a smooth burnisher would, viz. by laying the coating solidly down. This example is one where extreme nicety is needed, but the gilding or silvering of articles purely ornamental, may be effected with much less care and mechanical detail.

For depositing silver the power of the battery needs not to be very strong, in which case however, a soft deposit is formed; if it be required harder, it can be readily obtained by employing more power; but, on the other hand, too much will cause the metal to separate in a pulverulent form. The suspended silver pole should present a considerable surface towards the article to be coated.

The colour of the metal will be perfectly white, and with somewhat of a milky hue; the brush immediately burnishes this; but, if necessary, silver may be deposited perfectly bright and lustrous, by the addition of carbon disulphide to the solution, to the extent of about 6 drachms to the pint. The mixture must stand some days before using.

In depositing gold, the moment the article is immersed, it will be covered with a thorough coating, although, of course, excessively thin; but such a film would merely give colour, and not stand wear. Moreover, as this metal, in the pure state in which it is deposited, is naturally very soft, even after burnishing, the coating must be tolerably thick.

The deposit of gold may be considered good if, on removing the article, it appears of a brownish-yellow colour; this affords a burnished surface of the colour of pure gold; but here again, as in silver, a pulverulent deposit will result particularly from too much battery power, and this will be evidenced by the dark-brown colour of the metal when taken out of the cell.

It is often required to gild articles of iron or steel, but it is very difficult to get the metal adherent; and, although it will cover well, it rubs off by the least friction. In such a case a solid coating may be effected by first depositing a film of copper from the double cyanide, as described, which will become perfectly adherent upon the steel, after which the gold will also become firmly so upon the copper coat.

Platinum, and also palladium, may be deposited much in the same manner as gold, in both cases working the solutions warm. Palladium is tolerably easily worked. The solution for this may be made by dissolving palladium in aqua regia, evaporating, and after precipitating it by means of potassic cyanide, redissolving the precipitate in a small excess of the latter salt. A palladium anode is then used, with this solution in the decomposing cell.

Platinum is more difficult of deposition in the reguline form, and only to be effected by using a very weak battery power, with a small platinum anode; otherwise, if the power be at all strong, the metal is deposited as platinum black. Thus, on the other hand, the pulverulent metal is thrown down upon silver for the plates of Smee's battery, by using a tolerably strong battery power upon a double chloride of platinum and sodium, the salt being acidulated slightly with a little sulphuric acid.

In working platinum, as the metal of the anode is not taken into solution by the body evolved upon it, the platinum compound employed for electrolysis must be supplied to the solution from time to time, as the metal is deposited, and removed from it. One of the following solutions may be used: —

1st. A double chloride of platinum and sodium, made by combining atomic proportions of platinic and sodic chlorides. This salt is dissolved in water for use.

Or 2nd. An ordinary solution of platinic chloride may be precipitated by potassic cyanide, and the precipitate afterwards redissolved in slight excess of the latter.

Or 3rd. A solution of platinic chloride may be made equal to ten parts of metal; this is treated with ten parts of caustic potass.

The precipitate thrown down is then boiled in seventy of oxalic acid, and after filtering, thirty of caustic potass added to it.

The solution for depositing platinum should contain about half an ounce of the metal in 100 ounces of solution.

Nickel is now much employed for covering other metals, for the bright silvery surface afforded is but little altered by ordinary use. Hence it has come into considerable use for fine weights, and for coating mathematical and surgical instruments, and other ordinary purposes. The salt employed is the double sulphate of nickel and ammonium; but there is some uncertainty and difficulty in working it by the battery. A company is now carrying on the process of nickel plating in London.

Zinc, cadmium, tin, bismuth, and antimony, are all easily thrown down, but none of them have any practical importance.

Lastly, alloys, as brass, bronze, alloys of gold with silver, &c., may be deposited, but they are manipulated with more or less difficulty, and hence require much care in working. I have lately been engaged in the deposit of definite alloys of gold with silver, and have succeeded in depositing them identical in composition to that of the anode employed. For instance, with an anode of four parts of gold with one of silver I first made a solution for the decomposing cell of just these relative proportions, doing this by electrolysing potassic cyanide with a plate of fine gold and another of silver, as already described. The cell charged with this, and the anode immersed, a platinum cathode was used to deposit upon. On this a clean plate of the alloy was put by a four-cell Smee's battery. The colour of the plate was just the greenish one of the anode; 11·96 grains were removed after a time for examination, and dissolved in aqua regia, the gold solution carefully poured off and reduced, this gave 9·7 grains of gold. The silver was estimated from the residual chloride, which was well washed and carefully dried in a small flask and then weighed. The argentic chloride was next dissolved out by means of ammonia, and on weighing the empty flask just 3 grains of chloride were found to have been removed, corresponding to 2·26 of silver. This very nearly resembled the composition of the anode, viz., $\frac{1}{5}$th of silver to $\frac{4}{5}$ths gold. The difference in the silver between the 2·26 grains found and 2·42 the actual proportion, being no doubt due to loss in the manipulation.

A variety of materials have been employed for forming moulds, upon which, however, copper is usually first deposited. The non-conducting ones are formed of plaster of Paris, mixtures of stearine and wax, gutta percha, either alone or mixed with other plastic materials, together with some other compounds, the materials being selected according to the nature of the object to be moulded. All these require to have some conducting material over their surface for deposition upon, and the substance suggested by Mr. Murray, viz., good black-lead, is found to answer most efficiently.

In using plaster of Paris, the mould being taken in this material, is next rendered impervious to the metallic solution by placing it face upwards in a tray of melted wax. On watching it the wax will be seen to rise to the surface of the plaster by absorption through its texture. It is then removed, and, when cold, brushed carefully over with good black-lead, by means of a soft brush, and the conducting wire having been previously inserted, the plumbago is continued well on to this.

A good formula for a stearine compound is given by Mr. Watt. It is 8 oz. of stearine to 6 of wax and 1 of spermaceti. These are melted together, and then an ounce of plumbic carbonate is stirred in. The latter adds to the specific gravity of the mixture, and so prevents the tendency of the mould to float in the solution. It is used by melting it and pouring upon the object, care being taken to stir out air-bubbles, if formed.

Gutta-percha may be used alone, being softened by heat, but the surface of the work to be copied must be slightly greased with oil before its application. It is then kneaded over it, and when covered, a piece of wood is laid upon it, also greased to prevent adhesion, and upon all a weight. When cold it may be taken off. Moulds may thus be obtained in gutta-percha from plaster casts.

Mr. Gore mixes marine glue with the gutta-percha, in the proportion of one part of the former to two of the latter. The marine glue is melted in an iron ladle, and the gutta-percha then added in small pieces, and the two, when completely melted, are to be well mixed. Gore states that moulds of this material may be employed with care for several deposits; that it takes the plumbago better than gutta-percha alone, and in casting will receive a sharper impression, and is easily removable from the original.

APPENDIX.

THE very great variety of systems of weights and measures employed in various countries has been a great hindrance to scientific intercommunication of ideas ; and, as the records of the labours of men of various nations have become more universally circulated, so has the need been felt of some one common system of weights and measures, until it has at length led to a pretty general employment of the French metrical system in our laboratories, as also in scientific writings, and the gramme for weight, with the cubic centimetre and the litre for measure, have almost universally become the respective standards for each class of quantities.

In this excellent system the denominations of length, surface, capacity, solidity, and weight, are all formed from one fundamental standard, viz., from a measurement of a portion of the earth's circumference. This standard, the metre, is presumed to be a ten-millionth part of a meridian line, drawn from the pole to the equator. This is the lineal French metre, and is a measure slightly exceeding our English yard, for 1 metre equals 1·093633 yards.

For surface measure this metre is squared and the Are is the unit, and is equal to 100 square metres, or 119·6033 square yards ; but for smaller uses the square metre is subdivided decimally into the decimetre, centimetre, and millimetre.

Next, the square metre is cubed to obtain measures of capacity and of solidity. Then taking a cubic metre, and dividing it into

1 million parts, or in other words, taking the $\frac{1}{100}$th of the linear metre, and cubing that we get the cubic centimetre, and have a measure which, of distilled water at its maximum density, viz., at 4° Cent. will just equal 15·434 English grains. This weight is called the gramme, and constitutes the standard or unit of weight.

Lastly, 1000 cubic centimetres give the litre or unit of capacity. This just equals 1·7608 English pints.

The following are the various English corresponding quantities to the three principal denominations :—

Metrical unit: Metre = 1·093633 yard, or 3·2809 feet, or 39·3708 in.

Weight unit: Gramme = 15·434 grains, or 0·002204 pound.

Capacity unit: Litre = 0·220096 imp. gall., or 1·7608 imp. pint, or 61·02705 cubic inches.

Length Measures.	English Inches.	*Weight Measures.*	
Millimetre	·03937	Milligramme	·0154
Centimetre	·39370	Centigramme	·1543
Decimetre	3·93708	Decigramme	1·5434
METRE	39·37080	GRAMME	15·4340
Decametre	393·70800	Decagramme	154·3400
Hectometre	3937·08000	Hectogramme	1543·4000
Kilometre	39370·80000	Kilogramme	15434·0000
Myriometre	393708·00000	Myriogramme	154340·0000

Capacity Measures.

		Cubic Inches.
Millilitre	=	·061027
Centilitre	=	·610270
Decilitre	=	6·102705
LITRE	=	61·027051
Decalitre	=	610·270510
Hectolitre	=	6102·705100
Kilolitre	=	61027·051000
Myriolitre	=	610270·510000

The number of metals found in combination with chlorine in a native condition is very small. The chloride most abundant in quantity is that of sodium ; very extensive beds of sodic chloride are found at Northwich in Cheshire, also at Durham, in Ireland at Belfast. Then on the Continent in Spain and Poland.

2nd. Potassium and magnesium exist as a double chloride in the mineral carnallite (see p. 536), and this is not only worked for magnesium, but also for separation of its potassic chloride.

3rd. Silver is found in combination with chlorine as horn silver, this mineral as already stated (p. 152), forms the silver ore of the Chilian mines.

4th. Besides these, mercury is found as chloride or native calomel. This form known as horn quicksilver, is found in considerable quantity in the Idrian works.

Fletcher, of Warrington, has devised some very useful forms of gas apparatus for the smaller uses of the experimental laboratory. Of these his 'hot-blast blowpipe' may be first noticed. In this the second tube or blast is coiled round the jet, and below them are placed three small separate Bunsen burners, by which both the gas-jet and ingoing blast of air are heated up to a high temperature; by this means Fletcher has melted 3 oz. of gold when supported on pumice-stone.

This blowpipe may be used either with or without the hot blast.

For his 'double-jacketed furnace,' which he employs for melting purposes, as also with a small muffle, he uses a compound Bunsen of 55 jets, which, he says, is unapproached in heating power, for general purposes, by any burner not requiring a blast, which has yet been made, and that it will melt 3 to 4 ounces of cast iron in 35 minutes, used with a 3-ft. chimney. It consumes from 18 to 30 cubic feet of gas per hour, dependent upon length of chimney and draught.

In making iron assays by Penny's method (see page 417), too large a weight of ore is to be avoided, for some ores, especially some of the oxides, are not easy of solution in acid. Again, in the case of our black-band ores, the bituminous matter in them will not be dissolved, but remain suspended in the assay solution, and much hinder the operation.

The estimation of carbon in iron is made by converting it into carbonic anhydride, and collecting this as in ordinary operations of organic analysis, then from its amount calculating the quantity of carbon present. About 50 grains of the iron are taken in fine filings and mixed with about 500 of cupric oxide (or plumbic chromate), these are put in an ordinary combustion-tube, to one end of which is connected a Liebig's bulb potash tube, charged and weighed; to the other a tube for carrying in oxygen gas is attached. The combustion-tube is arranged in a combustion furnace and heated, beginning at the end next the potash apparatus, and carried gradually to the other end till it is all red hot, a stream of oxygen being slowly passed through at the same time. The operation over, the potash-tube is removed and weighed, and the carbon calculated from the amount of carbonic anhydride absorbed.

To determine the amount of uncombined carbon or graphite, another portion of iron is dissolved in hydrochloric acid, the solution filtered, and the residue washed with water, then with potash, and lastly with ether. It is then dried at 212° F. or 100° C., and weighed in a covered crucible. It is then burned, and there will be a portion of silica left unburned, which must be deducted from the weight found before burning; the loss, as shown by again weighing, is due to graphite or uncombined carbon. Then this deducted from the first carbon estimation by combustion, will leave the weight of combined carbon.

Silicon is estimated in iron by solution of a weighed quantity in hydrochloric acid. This is evaporated to dryness, then treated with a small quantity of strong hydrochloric acid, and afterwards with water, to dissolve soluble matters. The residue is filtered out and burned, to get rid of graphite. This latter residue is silica, from which the silicon is to be estimated.

Fresenius estimates sulphur in iron by acting on about 10 grammes in very fine division by hydrochloric acid in a flask furnished with a funnel safety tube for admission of the acid. Through the same cork passes a tube to two U tubes, which are filled with a strongly alkaline solution of lead; to the outer one of these a caoutchouc sucking-tube is attached. By this, acid is sucked from the funnel upon the metal in the flask. The latter is heated, and acid again drawn in from time to time till the iron is all dissolved. The evolved gas passes into the lead solutions, and plumbic sulphide is formed. Then to ensure all the evolved gas traversing the U tubes, an aspirator is at the last attached, so as to draw it all through. The plumbic sulphide is next collected on a filter, fused with sodic carbonate and nitre. Then treated with water, and carbonic acid passed in so as to throw down any dissolved lead. After filtering this out, the liquid is acidulated with hydrochloric acid, and from it the sulphuric acid, resulting from the sulphur contained in the metal, is estimated by precipitating by baric chloride, and from this baric sulphate the amount of sulphur is calculated.

Phosphorus in iron is estimated by conversion into phosphoric acid, and the following is a method by Fresenius which has been well modified by Spiller.*

Fresenius dissolves a weighed quantity of the metal in nitro-hydrochloric acid, and then adds sulphurous, so as to reduce the solution of the metal to a protosalt. Boils to expel excess of sulphurous acid, and when cool adds ammonia to partly neutralize, after which ammonic acetate is added, and the whole boiled. Thus the phosphoric acid is concentrated in a precipitate of basic ferric acetate, while nearly all the iron remains in solution as ferrous acetate, and thus the two are separable by filtration.

The precipitate filtered out is partly washed and dissolved in hydrochloric acid, then to the warmed solution first citric acid is added, next excess of ammonia, and then ammonio-hydric sulphide. Thus the iron is precipitated. This precipitate is to be washed with water containing some ammonio-hydric sulphide. The washings and filtrate are evaporated with exposure to air. Sulphur thus goes down and is separated, after which the liquid has mixed magnesic and ammonic chlorides added with free ammonia, the precipitate formed is ignited and weighed, and from the magnesic pyrophosphate the amount of phosphorus is calculated.

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* *Chem. Soc. Journal*, vol. xix. 1866, p. 148.

Spiller shortens the operation 'by dispensing with the acetic treatment, and states that for the purpose of concentrating the whole of the phosphoric acid contained in the solution of the specimen under examination in a comparatively small proportion of the ferric oxide, it is only necessary to add to the partially reduced and cold solution, aqueous sesquicarbonate of ammonia, until the precipitate, at first red, assumes a greenish hue,' showing ferrous carbonate to be thrown down. The whole of the phosphorus is shown by him, to be contained in this precipitate.

The liquid must not exceed 70° to 75° F. when the ammonic sesquicarbonate is added, or phosphate will be lost. And it is advisable to drop in a few pieces of solid ammonic carbonic into the flask after solution of the iron in 'red' nitro-hydrochloric acid. The effervescence produced will expel nitrous vapours. And the great excess of acid should be driven off by evaporation, and the diluted solution further neutralized with ammonia, or the carbonate, before adding the bisulphite of ammonia, to effect the reduction of the ferric chloride.

In all these iron analyses the operations require extreme care, for they are amongst the most difficult ones of chemical research.

The assay of zinc ores may be carried out either as an analysis, or by volumetric methods. Of the latter Fresenius gives a most complete account,* and out of several, that modified by Künzel from Schaffner's process is the one largely employed in the Belgian zinc works.

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* *Quantitative Analysis*, Fourth Edition, p. 653.

The testing solution is one of sodic sulphide prepared by dissolving the crystallized salt in water, in the proportion of 100 grammes to 1000–1200 water; or by supersaturating a soda solution by dihydric sulphide, and by either method subsequently diluting the solution, so that 1 cubic centimetre may precipitate about 0·01 gramme of zinc.

This solution is standardized by dissolving 10 grammes of chemically pure zinc in hydrochloric acid, or a corresponding quantity of pure zincic sulphate, or of crystallized double sulphate of zinc and potassium may be used. In either case the solution is made up to 1 litre with water. Each centimetre cube of this also equals 0·01 grain zinc.

Next 30–50 cubic cent. of this is to be measured into a beaker, ammonia is then added until the precipitate formed is redissolved, and it is next diluted to 400–500 cubic cent. with water.

Having filled a graduated burette with the sodic-sulphide solution, it is run in as long as a distinct precipitate is formed, and stirred well after each addition. A drop is removed, placed on a white porcelain slab, and spread out. Then a drop of pure nickel chloride is placed in the centre of the assay drop. If the edge of the nickel salt remains blue or green, the addition of sodic sulphide must be continued to the assay, testing from time to time until the drop of nickel chloride is surrounded with a blackish grey edge. The assay is now completed, for all the zinc is precipitated, and there will be a slight excess of sodic sulphide present. The exact depth of tint must be borne in mind, as the same has to be arrived at in the after actual assays, as indicative of their completion.

The complete precipitation of the zinc may be verified by the addition of a trace or so more of the reagent, which should darken in the salt proportionally. The whole experiment is to be checked by a second one; in this the whole amount of the reagent as first indicated may be run in at once, less 1 cubic cent.; and the assay then worked by 0·2 cubic cent. at a time till the exact reaction is arrived at. This last is a trustworthy experiment, and should give the exact value of the standard solution. But it is liable to speedy change, and hence requires frequent verification.

For the actual operation if the ore be rich 0·5 gramme is taken, but if poor 1 gramme. This is powdered, and dissolved in hydrochloric acid with a little nitric, using heat. The excess of acid is then evaporated away, and the residue diluted with water, and then supersaturated by ammonia. Filter into a beaker, wash with water containing some ammonia, and slightly warmed, until these washings are not rendered at all turbid on adding ammonio-hydric sulphide.

If the ore contain but little iron, the zinc left in the hydrated ferric oxide is not enough to need caring for; but if much iron is present, then after evaporation of the greater part of the acid solution, the liquid is nearly saturated by a dilute solution of sodic carbonate, and the iron afterwards precipitated by sodic acetate, the liquid is boiled, filtered, and the precipitate washed; the washings are concentrated and added to the filtrate, and the whole treated by ammonia till the precipitate first formed is redissolved.

If manganese is also present, for accurate results, it must be separated by passing in chlorine to the solution, after the iron has been precipitated by sodic acetate.

If the ore contained lead, sulphuric acid must be added to the acid solution during evaporation; when finished, the residue is exhausted by water and filtered, and the operation then carried on as before.

The actual assay operation is worked just as the one described for standardizing the solution, and the double or check assay should be made in the same way, viz. by adding to within 1 CC. of the reagent solution, and finishing carefully by 0·2 CC. at a time till correct. The proportion of standardized solution consumed in the assay will correspond in amount to that of the zinc contained in the ore under examination.

INDEX.

Acid antimonic, 389
  arsenic, 405
  arsenious, 403
  bismuthic, 345
  chromic, 399
  ferric, 469
  manganic, 478
  metastannic, 500
  permanganic, 478
  renewal of, in voltaic battery, 561
  salts, 53
  stannic, 499
  sulpharsenic, 405
  titanic, 396
Adit level, 28
Affinity, 35
  chemical, 35
Aich metal, 520
Alberti's reduction of poor mercurial ores, 132
Alcohol blast lamp, 82
Alloying, use and object of, 63
  malleability, ductility, and tenacity, affected by, 63
  specific gravity affected by, 64
Alloys, 61
  crystallization of, 65
  fusing points of, 65
  Matthiesen's definition of, 62
  oxidizability of, 64
  solidifying and fusing points, 67
Almaden mercury reduction, 133
Alumina, 533
  discrimination, 534
  estimation of, 535
Aluminic silicate, 533
Aluminium, 529
  alloys with copper, 533
    silver, tin, and zinc, 533
  properties, 531
  solder for, 532
Amalgam copper, 378
  gold, 267
  lead, 338
  native, 153
  palladium, 309
  platinum, 304
  silver, 179
  tin, 502
Amalgamation of zinc for electric uses, 549
Amethyst colouring oxide of, 477
Analysis, alloyed gold, 272
  amalgam of copper, 382
  amalgam silver, 187
    tin, 509
  bismuth and copper, 350
    and lead, 349
  brass, 523
  bronze, 524
    Church's, 521
  copper pyrites, 474
  fusible metal, 508
  German silver, 525
  gold, silver, and platinum, 305

Analysis, solders, 508
Anhydride, antimonic, 389
  arsenic, 405
  arsenious, 403
  bismuthic, 345
  chromic, 399
  titanic, 396
Annabergite, 484
Anode, 553
Anthracite, 111
Antimonial silver, 153
Antimony, 384
  alloys, 390
  butter of, 389
  estimation of, 391
  ores, 384
  preparation of pure, 387
  properties, 387
  reduction, 386
  regulus of, 386
  tests for, 390
  working at Malbose, 385
Antimonic acid, 389
  chloride, 389
  sulphide, 390
Antimonious oxide, 388
  chloride, 389
  sulphide, 389
Argentic bromide, 177
  carbonate, 179
  chloride, 176
  iodide, 177
  nitrate, 178
  oxide, 176
  sulphate, 179
  sulphide, 177
Argentiferous galena, 312
Argentous chloride, 176
  oxide, 175
Arrastre, 159
Arsenic, 402
  alloys, 405
  acid, 405
  discrimination, 405
  detection in metallic copper, 408
  estimation, 408
  Marsh's test for, 407
  sesquioxide, 403
Arseniates, 405
Arsenic anhydride, 405
Arsenical pyrites, 402
Arsenious anhydride, 403
Arseniuretted hydrogen, 407
Assay balance, 200
  furnace, 192
  pound, 204
  tools, 199
  weighings, trade for gold, 277
  weights for silver, 204
    for gold, 277
Assay of auriferous pyrites, 275
  bronze, 524
  copper, 353
    by wet methods, 354
  Dumonte's wet of lead, 315
  gold alloys, 275
    by blowpipe, 287
  gold containing platinum, 306
  gold quartz, 273
    Matthey's apparatus for, 284
  iron ores, 413
    wet, 415
    Penny's, note on, 574
  lead ores, 313
  silver ores, 187
    alloys, 191
      wet, 209
Atomic weights of elements, 4
Aurates, 263
Aurous chloride, 264
  iodide, 265
  oxide, 263
  sulphide, 265
Auric chloride, 264
  iodide, 265
  oxide, 263
  sulphide, 265
Axes of symmetry, 58

BALANCE assay, 200
  Black's, 288
  specific gravity, 19
Bar tin, 497
Baric reactions, 545
Battery stamp for gold, 235
  Bunsen's, 554
  Daniell's, 555
  Grove's, 554
  Smee's, 554
Bauxite, 531
Bean shot copper, 375
Beating of gold, 260

- Bell's method for aluminium, 531
- Bell metal, 506
- Bellows table, 88
- Berthier's plan of estimating heating power of fuels, 121
- Berthollet's division of salts, 53
- Berzelius, alloy of Pt, Cu, and Zn, 518
- Bessemer's iron process, 452
    - steel process, 453
- Binary theory of salts, 54
- Birkmyre's copper process, 367
- Bismuth, 342
    - alloy with copper, 380
        - gold, 347
        - lead, 347
        - palladium, 347
        - platinum, 347
        - silver, 347
    - amalgam, 346
    - discrimination of, 347
    - estimation of, 348
    - localities, 342
    - metallurgy of, 342
    - ores, 342
    - preparation of pure, 344
    - properties, 344
    - sesquioxide, 346
- Bismuthic acid, 345
    - chloride, 346
    - sulphide, 346
- Black-band iron ores, 412
    - flux, 183
- Black-lead crucibles, 104
- Blast-furnace copper, 370
    - cinder, 431
        - analysis of, 432
    - Deville's, 99
    - Faraday's, 97
    - Griffin's gas, 91
    - iron, 423
        - working of, 429
    - lead, 322
    - Sefstrom's, 97
    - tin, 496
    - gases, 432
- Blende, 510
- Blistered copper, 363
- Block-tin, 497
- Blowing cylinder (iron blast), 426
- Blow-pipe, 83
    - assaying by, 287
- Blow-pipe, Black's, 84
    - examinations, 87
    - flame, oxidizing, 85
        - reducing, 86
    - Herapath's, 90
    - oxyhydrogen, 91
    - reagents, 86
    - supports, 86
    - table and bellows, 89
    - use of, 85
- Blue metal (copper), 362
- Bog-iron ore, 412
- Bohemian potash glass, 543
- Bone-ash, 191
- Borax, 182
- Brasqued crucibles, 106
- Brass, 518
    - by cementation, 518
    - analysis of, 523
- Bricks P. P. 103
    - Dinas, 101
    - ordinary building, 103
    - Stourbridge, 103
- Britannia metal, 505
- Bromides, metallic, 46
- Bronze, 506
    - analysis of, 524
        - Church's, 521
    - Mint assay of, 524
- Brown's wet assay of copper, 356
- Brystrom's pyrometer, 123
- Buddle, 32
- Bunsen's gas-burners, 70
- Burnett's solution, 517
- Butter of antimony, 389

- Calamine, 510
- Cadmium, 525
    - alloys, 527
    - dry method for, 526
    - estimation, 528
    - properties, 526
    - Stromeyer's method for, 526
    - tests for, 527
- Cadmic oxide, 527
    - sulphide, 527
- Calcined coarse metal (copper), 362
- Calcium reactions, 545
- Calomel, 143
- Calvert's plan for separation of sulphur in iron working, 429

Calvert on separation of gold from quartz, 241
Carbon in iron and steel, 444
    estimation of, 574
Case-hardening, 462
Castilian furnace (lead), 324
Cast-iron, 433
    steel, 448
Catalan iron process, 421
Cathode or negative pole, 553
Cement copper, 374
Cementation of steel, 446
    brass, 518
Chalcolite, 393
Charcoal, 114
Chemical and mechanical union, difference of, 34
    combination, laws of, 36
Chemical affinity, 35
Chilled castings, 462
Chinese vermilion, 144
Chlorides. metallic, 43
    native, 573
    preparation of, 44
    reduction, 45
Chrome, 398
    iron ore, 398
Chromic acid, 399
    oxide, 399
Chromium, 398
    discrimination, 400
    pink oxide, 400
    protoxide, 399
    sesquioxide, 399
Chromous oxide, 399
Church, analysis of native silver, 151
    of bronzes, 521
Cinnabar, 129
    analysis of varieties of, 144
Clay-band ore, 412
Clays, Dinas, 101
    Ewell, 101
    fire, 99
    Monmouth, 101
    Newcastle, 100
    ordinary building brick, 103
    Pembroke, 101
    pipe, 534
    porcelain, 534
    potters, 534
    Stourbridge, 100
Cleaning articles before receiving electro deposits, 562
Coal, anthracite, 111
    ash of, 111
    Cannel, 110
    Devon, 110
    hard, 110
    Newcastle, 110
    products of distillation of, 110
    Staffordshire, 110
Coarse metal (copper), 361
Cobalt, 480
    blue, 482
    blue oxide, 481
    discrimination, 483
    estimation, 483
    metallic, 480
    ores, 480
    oxide, 481
    prepared oxide, 481
    properties, 480
    silicate, 482
    uses, 476
Cock for wet silver assays, 213
    upon palladium working, 307
Coke, 114
    from gas-tar, 118
    ovens, 118
Coking in heaps or mounds, 117
Cold-blast iron, 428
Comparison of fuels, 119
Condie's steam-hammer, 441
Conditions influencing electro deposits, 560
Conducting or negative plate, 552
    wire, magnetic condition of, 549
Copper, 351
    alloy with bismuth, 380
            gold, 380
            palladium, 380
            platinum, 380
            silver, 379
            zinc, 518
    amalgams, 378
    assay of ores, 353
    Birkmyre's method for, 367
    blistered, 363
    commercial, impurities in, 374
    discrimination, 381
    estimation, 382

- Copper, fumes evolved in ore-roasting, 358
  - grey ore, 552
  - glance, 352
  - Henderson's plan of reduction, 368
  - indigo ore, 352
  - kernel roasting, 368
  - localities, 351
  - Napier's method of reduction, 367
  - native, 352
  - ores, 352
  - poling, 365
  - production of pure, 375
  - properties, 375
  - protosulphide, 378
  - protochloride, 378
  - protoxide, 377
  - purple ore, 352
  - pyrites, 352
  - reduction by blast furnace, 369
  - reduction at Swansea, 357
  - refining, 364
    - at Mansfeld, 372
  - smelting in Sweden and Norway, 374
  - subchloride, 378
  - suboxide, 376
  - subsulphide, 378
- Copperas, 471
- Crookes' amalgams for gold, 240
- Crown glass, 543
- Crucibles, brasqued, 106
  - Cornish, 105
  - French, 105
  - Hessian, 104
  - London, 105
  - metallic, 107
  - plumbago, 104
  - tested, 107
- Crum's test for manganese, 479
- Crystals, cleavage of, 57
  - dimorphism of, 58
  - isomorphism, 58
  - secondary forms of, 57
  - water of constitution in, 59
- Crystallization, 56
  - by subliming, 60
  - of metals, 60
  - water of, 58
- Crystalline axes, 57
- Crystalline axes, influence of light on, 60
- Cullet, 544
- Cupels for large operations, 170
  - small, 191
  - furnace for refining, 169
    - assaying, 192
  - mould, 191
- Cupellation operation on large scale, [172
  - operation on Continent, 174
  - on small scale, 191
    - rationale of, 209
  - of silver, 206
  - of gold, 279
    - by blowpipe, 287
  - platinum, 298
  - theory of, 172
- Cupreous chloride, 378
  - oxide, 376
  - sulphide, 378
- Cupric arsenite, 404
  - chloride, 378
  - oxide, 377
  - sulphide, 378

- Daniell's pyrometer, 124
- Decimal solution of salt, 212
  - silver, 212
- Decrepitation, 59
- Decomposing cell, 559
  - use of metallic salt in, 559
- Deliquescence, 59
- Dental gold leaf, 263
- Deville's blast furnace, 99
  - method of platinum working, 297
- Dinas clay, 101
- Diarsenic pentasulphide, 405
- Dodd's assay of silver, 218
- Dolomite, 536
- Double cyanide potassium and copper, 561
  - salts, 56
  - sulphate of nickel and ammonium, 567
- Ductility of metals, 9
- Dutch metal, 520
  - vermilion, 145

- Efflorescence, 59
- Eisen-nickelkies, 484
- Electric conduction, 17

Electric current action of, on magnet, 549
  decomposition in atomic proportions, 550
  local currents, 551
  order of metals, 552
Electro deposits of alloys, 567
  cleansing work for, 561
  of copper, solution for, 561
  of gold and silver, 562
  gold or silver, solution for, 563
  Ladd's manipulation, 564
  moulds for, 568
  of nickel, 567
  platinum and palladium, 566
  power of battery for, 565
  rate and texture controlled, 560
  solutions for steel, 561
  on steel, 561
  by single cell, 558
  by battery, 559
  temperature for, 564
Electro metallurgy, 548
Electrolysis, bodies capable of, 553
Electrotype, origin of, 556
Elements, 1
  metallic, table of, 4
  non-metallic, 7
Emerald nickel, 484
Equivalent, 36
Ewell clay, 101

Faraday's blast furnace, 97
  thin gold films, 258
Feathered shot copper, 375
Ferric acid, 469
  chloride, 470
  oxide, 469
  sulphate, 471
  sulphide, 470
Ferrous carbonate, 471
  chloride, 470
  oxide, 469
  sulphate, 471
  sulphide, 470
Finery cinder, iron, 436
Fine metal (copper), 362
Fire-clays, 99
Flame, analysis of, 84
  blowpipe oxidizing, 85
    reducing, 86
Fletcher's gas blowpipe, 573
Flint glass, 544
Fluxes, 182
Forging platinum, 295
Fowler's solution, 404
Fuels, 109
  comparison of, 119
  determination of heating power, 120
Fulminating gold, 264
  silver, 176
Furnaces, 68
  Deville's platinum, 299
    blast, 99
  Faraday's blast, 97
  Gore's gas, 72
  Griffin's blast, 91
    cupelling, 196
    melting, 74
  iron blast, 423
  muffle, 192
  Puddling, 438
  reverberatory, 95
  Sefstrom's, 97
  Siemens' regenerative, 79
  Watson's, 197
  Wind, 92
Fusible metal, 504
    analysis of, 508

Galena, 312
  analysis of, 341
  argentiferous, 312
Galvanic battery, 552
    Bunsen's, 554
    Daniell's, 555
    Grove's, 554
  causes of cessation of action in, 554
  decomposing effect of, 553
  diminished action renewed, 561
  poles of, 553
  Smee's, 554
  Watt's, 557
Galvanised iron, 522
Galvanometer, 550
  use of for electro depositing, 560
Gas-burners, 70
  from Siemens' producer, analysis, 78
  parting apparatus, 280

Gay Lussac's humid assay of silver, 209
Gedge's metal, 520
Generating plate, 549
German silver, 521
  analyses of, 525
Gilding, electro, 562
  on iron and steel, 561
  water, 268
Glass, 543
Goadby's fluid, 144
Gold alloys with antimony, 390
    copper 380
    lead, 339
    palladium, 269
    platinum, 269
    silver, 268
    tin, 503
    zinc, 518
  amalgamation of, 236
  amalgam, 268
    Crookes', 240
    Wurtz's, 240
    distillation of, 238
  American cementation of, 243
  analyses of Australian of, 223
    Californian, 224
    Welsh, 225
    alloyed, 272
  artificial crystallization, 259
  assay of alloys, 275
    blowpipe, 287
    of ores, 273
  associate metals, 221
  beating, 260
  blanket board, 236
  brittle, 270
  chlorides, 264
  coin, British, 380
    Foreign, 380
  containing iridium, 252
  cradling, 230
  crystals, 222
  digging, 230
  discrimination, 271
  estimation, 271
  Faraday's films, 258
  fine, commercial values of, 248
  how found, 221
  identity of composition, 223
  iodides, 265
Gold localities, 224
  melting, 239
  oxides, 263
  parting of, 280
    assay, 286
    Matthey's apparatus for, 283
  precipitants for, 254
  precipitation by ferrous sulphate, 257
    oxalic acid, 256
    sulphurous acid, 257
  preparation of pure, 252
  properties, 257
  quartz, crushing, 234
  refining, 243
    by Miller's chlorine process, 248
    by nitric acid, 245
    sulphuric, 246
  separation from mercury, 272
  solutions of, by battery for electro depositing, 563
  sulphides, 265
  uses of alloying, 270
  washing by pan, 233
    sluice, 233
Gramme, 572
Great Comstock mine, 154
Greenockite, 525
Gore's material for electro moulds, 568
Gun metal, 506
Gutta-percha for electro moulds, 568

HÆMATITE brown, 412
    red, 412
Haloid salts, 54
Hähner's mercury furnaces, 135
Heating apparatus, 68
Heat, measurement of, 123
Henderson's copper process, 368
Hessian crucibles, 104
Hot blast for iron, 427

IDRIAN mercury reduction, 130
  plan of reducing poor mercury ores, 132
Iodides metallic, 46
Iron alloys, 472
  assay English, 414
    Margueritte's, 418

- Iron assay, Penny's, 416
    - Swedish, 413
    - fluxes for, 414
    - note on, 574
  - bisulphide, 470
  - blast furnace, 423
    - cinder, 431
    - formation of potassic cyanide in, 433
    - gases, 432
    - working of, 429
    - blowing cylinders, 426
  - calcination of ore, 422
  - carbonate, 471
  - discrimination of ferric salts, 473
    - of ferrous salts, 472
  - dry puddling, 439
  - estimation of, 473
    - carbon in, 574
    - phosphorus, 575
    - silicon, 574
    - sulphur, 575
  - finery cinder, 437
  - flux in smelting, 429
  - fuel used for reduction, 428
  - grey cast, 420
  - hot blast arrangements, 427
    - statistics, 428
  - magnetic oxide, 470
  - merchant bar, 441
  - mottled cast, 420
  - native, 410
  - ores, 411
  - persulphate, 471
  - pig boiling, 440
    - composition and qualities, 433
  - preparation of pure, 466
  - properties, 467
  - protochloride, 470
  - protosulphate, 471
  - protosulphide, 470
  - protoxide, 469
  - puddled bar, 441
  - puddling, 438
    - furnace cinder, 442
  - refining, 435
  - reheating furnace, 442
  - smelting, 421
  - sesquichloride, 470
  - sesquioxide, 469
- Iron, separation from alumina, 474
    - from copper, 474
  - white cast, 420
- Iserine, 396
- Isomorphism, 58

- Kaolin, 534
- Kerl, table of heating power of fuels, 121
- Kermes' mineral, 390
- Kernel roasting (copper), 368
- Kupfernickel, 484
- Kyanising, 144

- Lamp spirit blast, 84
- Lead, action of water on, 334
  - alloy with antimony, 505
    - bismuth, 504
    - copper, 380
    - gold, 339
    - palladium, 339
    - platinum, 339
    - silver, 339
  - amalgam, 338
  - alloys with tin, 503
    - zinc, 518
  - assay of ores, 313
    - wet, 315
  - chloride, 337
  - chromates, 338
  - desilverizing, 328
    - Pattinson's plan of, 328
    - Parkes', 331
  - dioxide, 337
  - discrimination, 340
  - improving or softening, 325
  - metallurgy of, 316
  - ores, 312
  - presence in commercial copper, 366
  - properties, 333
  - protoxide, 335
  - pure, preparation of, 333
  - red oxide, 336
  - reduction of oxide, 331
  - smelting in blast furnace, 321
    - Castilian furnace, 325
    - ore hearth, 319
    - reverberatory, 316
  - smoke, 327
  - suboxide, 335

Lead, sulphide, 337
Lignite, 110
Limestone as an iron flux, 429
Lithium reactions, 547
Litre, 572
Local currents, 551
Longmaid's method of separation of gold from quartz, 242
Louyet's nickel process, 486
Lutes, 101
    plaster of Paris, 102
    Willis's, 102

Magistral, 160
Magnesia, 539
Magnesic oxide, 539
    chloride, 539
Magnesite, 536
Magnesium, 536
    alloys, 538
    amalgam, 539
    Deville's method for, 537
    properties, 537
    purification, 537
    Sonstadt's, method for, 537
Magnet affected by electric currents, 549
Magnetic oxide of iron native, 411
        artificial, 470
Malleability of metals, 9
Manganese, 476
    Crum's test for, 479
    discrimnation, 478
    estimation, 479
    preparation of metal, 476
    red oxide, 478
    separation from iron, 479
    sesquioxide, 478
Manganic acid, 478
    dioxide, 477
Manganous oxide, 477
Mansfeld, reduction of copper ores at, 370
    refining operations, 372
Margueritte's assay of iron, 418
Marsh's test, 407
Marl, 534
Massicot, 335
Matthey's parting apparatus, 284
Matthiesen's plan for casting wires, 13
Mercury, 128
    adulteration of, 138
    Alberti's operation for poor ores, 132
    Almaden, reduction at, 133
    chlorides of, 142
    Deux Ponts, reduction at, 136
    discrimination of, 146
    estimation, 147
    filtration of, 140
    Hähner's furnaces for, 135
    Horrowitz, reduction at, 136
    Idria, reduction at, 130
    impurities in commercial, 137
    iodides, 144
    Lansberg reduction process, 136
    native, 129
    ores, 129
    oxides of, 141
    properties, 140
    purification by digestion, 139
        Priestly's plan, 140
        redistillation, 140
    sulphides of, 144
Metallurgy, definition of, 1
Metallic alloys, 61
    bromides, 46
    chlorides, 43
        analysis of, 52
    iodides, 46
    lustre, 8
    opacity and transparency, 8
    ores how deposited, 27
    oxides, 37
        analysis of, 51
    phosphides, 50
    salts, 53
    selenides, 50
    sulphides, 46
        analysis of, 52
    veins and lodes, 28
Metalloids, 8
Metals, ancient, 2
    annealing of, 16
    base, 4
    chemical character of divisions of, 4
    colour, odour, and taste of, 9
    conduction of heat in, 16
        electricity, 17

Metals, conditions modifying, 17
    means of measuring, 17
  definition of, 8
    soft and hard, 15
  division and classification of, 4
  elasticity of, 16
  fusing points of, 16
  how found, 26
  heavy and light, 24
  malleability, ductility, and tenacity, 9
  noble, 7
  specific gravity of, 18
    means of taking, 19
Metastannic acid, 500
Metre, 572
Metrical system, 571
Millerite, 484
Mines, 27
  drainage of, 28
  sections of, 27
Mint muffle, 195
Mispickel, 402
Mosaic gold, 520
Muffle furnace for solid fuels, 192
  Griffin's gas, 196
  Watson's gas, 198
Muntz metal, 520

Napier's reduction of copper, 367
Neutral salt defined, 53
Nevada mines, 154
Newcastle clay, 100
Nickel, 484
  alloys, 488
  analyses, 522
  Berthier's method for, 485
  chloride, 488
  Cloez's method for, 486
  Deville's method for pure, 487
  discrimination of, 489
  estimation of, 490
  Louyet's method for, 486
  ores, 484
  oxides, 488
  preparation of metal, 485
  properties, 487
  separation from cobalt, 490
    copper, 525
  silver, 521
  sulphides, 488
Nickel, Thompson's method for, 486
Normal salt solution, 211

Ochre, 412
Odling on detection of arsenic in copper, 408
Ore crushing, 31
  jigging, 32
  stamping, 31
  washing, 31
Orpiment, 405
Oxides metallic, 37
    native, 38
  preparation, 38
  reduction, 40
Oxidizing flame (blow-pipe) 85

Palladium, 307
  alloy with bismuth, 347
    copper, 380
    gold, 310
    lead, 339
    platinum, 310
    silver, 310
    tin, 503
  amalgam, 309
  chlorides, 303
  discrimination of, 310
  estimation, 311
  oxides, 309
  preparation of, 307
  properties, 308
  sources, 307
Parkes' copper assay, 354
  lead-desilverizing operation, 331
Parting of gold, 245
  assays, 286
  in ordinary assays, 280
    containing platinum, 306
Patent yellow, 338
Pattinson's process, 328
Patio process, 158
Peat, 114
Pelouze's copper assay, 356
Permanganic acid, 478
Pewter, 504
  solder for, 505
Phosphides, 50
Phosphorus in iron, 419
  estimation of, 575
Pig-boiling, 440

Pig-iron, 430
Pimple metal (copper), 362
Pitchblende, 393
Plaster of Paris lute, 102
    moulds, 568
Plata-pina, 162
Plate-glass, 544
Plumber's solder, 504
Platinum, 291
    alloy with bismuth, 347
        copper, 380
        gold, 304
        lead, 339
        palladium, 307
        silver, 304
        tin, 503
        zinc, 518
    amalgam, 304
    associate metals with, 292
    black, 301
    chlorides, 303
    cupellation on large scale, 298
    Deville's method of working, 297
    discrimination, 305
    estimation, 305
    history of, 291
    localities, 291
    melting, 300
    oxides, 303
    properties, 302
    pure, 296
    refining, 298
    sulphide, 304
    vessels made by pressure, 302
    welding, 302
    Wollaston's method for, 293
Plattner, separation of gold from arsenical pyrites, 243
Plumbic dioxide, 337
    chloride, 337
    oxide, 335
    sulphide, 337
Poles of battery, 553
Polar condition of particles in voltaic circuit, 550
'Poling' copper, 365
Porcelain clay, 534
Potassic cyanide in iron blast furnaces, 433
    dichromate, 398
    ferrate, 469
Potassic permanganate, 418
Potassium, 540
    preparation, 541
    properties, 542
Pottery, 533
P. P. bricks, 103
Psilomelane, 476
Puddling, 438
    dry, 439
Purple of Cassius, 266
Putty powder, 500
Pyrites, 413
    magnetic, 413
Pyritic quartz treated for gold, 242
Pyrolusite, 476
Pyrometer, Brystrom's, 123
    Daniell's, 124
    Prinsep's, 123
    Siemens', 125
    Wedgwood's, 127

QUARTATION, 245
Queen's metal, 505

REACTIONS of metals of first and second division, 545
Realgar, 405
Red silver ore, 153
Reducing-flame (blow-pipe), 86
Reduction of silver from Miller's refining process, 250
Red shortness in iron, 419
Refining of gold by acids, 244
    by Miller's process, 248
    iron, 435
    lead, 325
    platinum, 299
    silver, 169
Regenerative furnace, 76
Regnault's analysis of refined and unrefined irons, 437
Reinch's test for arsenic, 306
Reverberatory furnace, 95
Ridsdale's process for separating iridium and osmium from gold, 252
Rinman's green, 482
Rouge, 469
Ruby, 533
Rumford's calorimeter, 121
Rutile, 396

- SALTS, binary theory of, 54
  - classification of, 54
  - crystallization of, 56
  - double, 56
  - normal, 54
  - solubility of, 59
  - sulphur, 55
- Sandiver, 545
- Sapphire, 533
- Scheele's green, 404
- Scorification, 189
- Sefstrom's blast furnace, 97
- Selenides, metallic, 50
- Shaft of mine, 28
- Shingling, 441
- Siemens' gas producer, 77
  - pyrometer, 125
  - regenerative furnace, 79
    - comparative cost of working, 81
    - temperature of working, 82
- Silicon in iron, 419
  - estimation of, 574
- Silver, 150
  - alloy with bismuth, 347
    - copper, 379
    - gold, 268
    - lead, 339
  - alloyed with palladium, 310
    - platinum, 304
    - tin, 503
    - zinc, 517
  - amalgams, 179
    - native, 153
    - analysis of, 187
  - amalgamation, hot, 162
    - Mexican plan, 158
    - Nevada, 168
    - Saxon, 163
  - ammonio-nitrate, 306
  - assay of ores, 188
    - alloys, 191
    - humid, 209
    - Indian method, 218
  - bromide, 177
  - carbonate, 179
  - chlorides, 176
  - cupellation on large scale, 169
    - small scale, 205
  - deposition by battery, 562
- Silver, of bright, 565
  - discrimination, 185
  - estimation, 185
  - iodide, 177
  - native, 151
    - Church's analysis of, 151
  - nitrate, 178
  - ores, 152
  - oxides, 175
  - parting assays of, 286
  - Plata-pina, 162
  - precipitation by copper, 180
    - iron, 180
  - properties, 174
  - pure, 179
  - quality obtained by cupellation, 173
  - reduction by Augustin's process, 156
    - Percy and Von Patera's process, 157
    - Ziervogel's process, 156
    - of chloride, 180
  - separation from copper ores at Mansfeld, 155
  - spitting or vegetation of, 174
  - sulphate, 179
  - sulphide, 177
    - Mexican, 152
      - Phillips' analysis of, 152
- 'Silvering' on glass, 502
- Simple circuit, action taking place in, 550
  - definition of, 551
- Slag lead, 324
- Slimes, 32
- Smalt, 481
- Sodium, 541
  - properties, 543
- Solder for aluminium, 532
  - brass, 520
  - German silver, 522
  - gold, 505
  - pewter, 505
  - plumbers', 504
  - silver, 505
- Spathose ore, 412
- Specific gravity, 18
  - of alloys, 25
  - balance, 19
  - bottle, 21

Specific gravity, calculation of, 20
  table of, 24
  temperature for taking, 23
Specular iron ore, 412
Speculum metal, 506
  analysis of, 524
Speiss, 484
Spiegel-eisen, 434
  analysis of, 435
Stannic chloride, 501
  acid, 499
  oxide, 499
  sulphide, 502
Stannous chloride, 501
  oxide, 499
  sulphide, 502
Steel, 443
  alloyed with other metals, 455
  amount of carbon in, 444
  analyses, 444
  annealing, 465
  Bessemer, 452
  blistered, 448
  cast, 448
  casting operation, 448
  cementation, theory of, 445
    operation, 446
  discrimination from iron, 466
  double shear, 448
  employment of spectroscope in making, 456
  formation of, 445
  hardening, 456
    cooling for, by mercury, 459
    increase in bulk by, 461
    plans for cooling for, 459
    temperature for, 458
  Heaton's, 456
  Huntsman's, 450
  Krupp's castings, 450
  Price and Nicholson's, 451
  puddled, 450
  Siemens', 451
  shear, 448
  Taranaki, 455
  tempering, 463
  tilted, 448
  Uchatius', 451
  welded to iron, 465
Stourbridge bricks, 103
  clay, 100
Strontium reaction, 545
Sulphides, 46
Sulphides, native, 46
  preparation of, 46
  reduction of, 49
Sulphur in iron, 419
  estimation of, in iron, 575
  salts, 55
Sump of mines, 28
Symbols of elements, 4

Tables, humid assay of silver, 217
  metrical system, 572
Taranaki sand, 411
Temperatures, measurement of high, 123
Tempering steel, 463
Tenacity in metals, 9
Thenard's blue, 482
Tin, 491
  alloy with antimony, 505
    bismuth, 504
    copper, 505
    gold, 503
    lead, 503
    lead, bismuth, and cadmium, 504
    palladium, 503
    platinum, 503
    silver, 503
  amalgam, 502
  analysis of, 509
  bar, 497
  block, 497
  chlorides, 501
  discrimination of, 507
  estimation of, 507
  history, 491
  impurities in commercial, 497
  metallurgy of, 491
  ores, 491
  oxides, 499
  plate, 506
  preparation of pure, 497
    electric action, by, 498
  properties, 498
  pyrites, 491
  refining of, 496
  roasting of ore by Brunton's calciner, 493
  smelting by blast furnaces, 496
    in reverberatories, 495
  stone, 491
  treatment of ores containing tungsten, 494

Titanic acid, 396
    anhydride, 396
    dioxide, 396
    nitride, 396
Titanium, 396
    discrimination, 397
Touchstone, assay by, 275
Turner's yellow, 338
Type metal, 505

UMBER, 412
Uranic nitrate, 394
Uranite, 393
Uranium, 393
        oxides, 395
        preparation of metal, 394
Ure's apparatus for distillation of mercury, 136

VARVICITE, 476
Vermilion, 144
    adulterations of, 146

WAD, 476
Water gilding, 208
Wedgwood pyrometer, 127
White lead, 338
        metal (copper), 362
Wind furnace, 93
Wire drawing, 10
Wolfram, 491
    treatment of ores, 494

Wollaston's micrometer wire, 12
    method of working platinum,
Woods, 112
    ash of, 114
    specific gravity of, 113
Wood's metal, 505
    analysis of, 509
Wurtz's amalgam, 240

ZAFFRE, 480
Ziervogel's separation of silver, 15
Zinc, 510
    alloy with copper, 518
    copper and platinum, 518
        gold, 518
        iron, 522
        lead, 518
        platinum, 518
        silver, 517
    amalgam, 517
    assay of ores, 577
    chloride, 517
    discrimination, 523
    distillation by Belgian plan, 5
        English, 511
        Silesian, 514
    estimation, 523
    ores, 510
    oxide, 516
    preparation of pure, 515
    properties, 516
    sulphide, 517

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